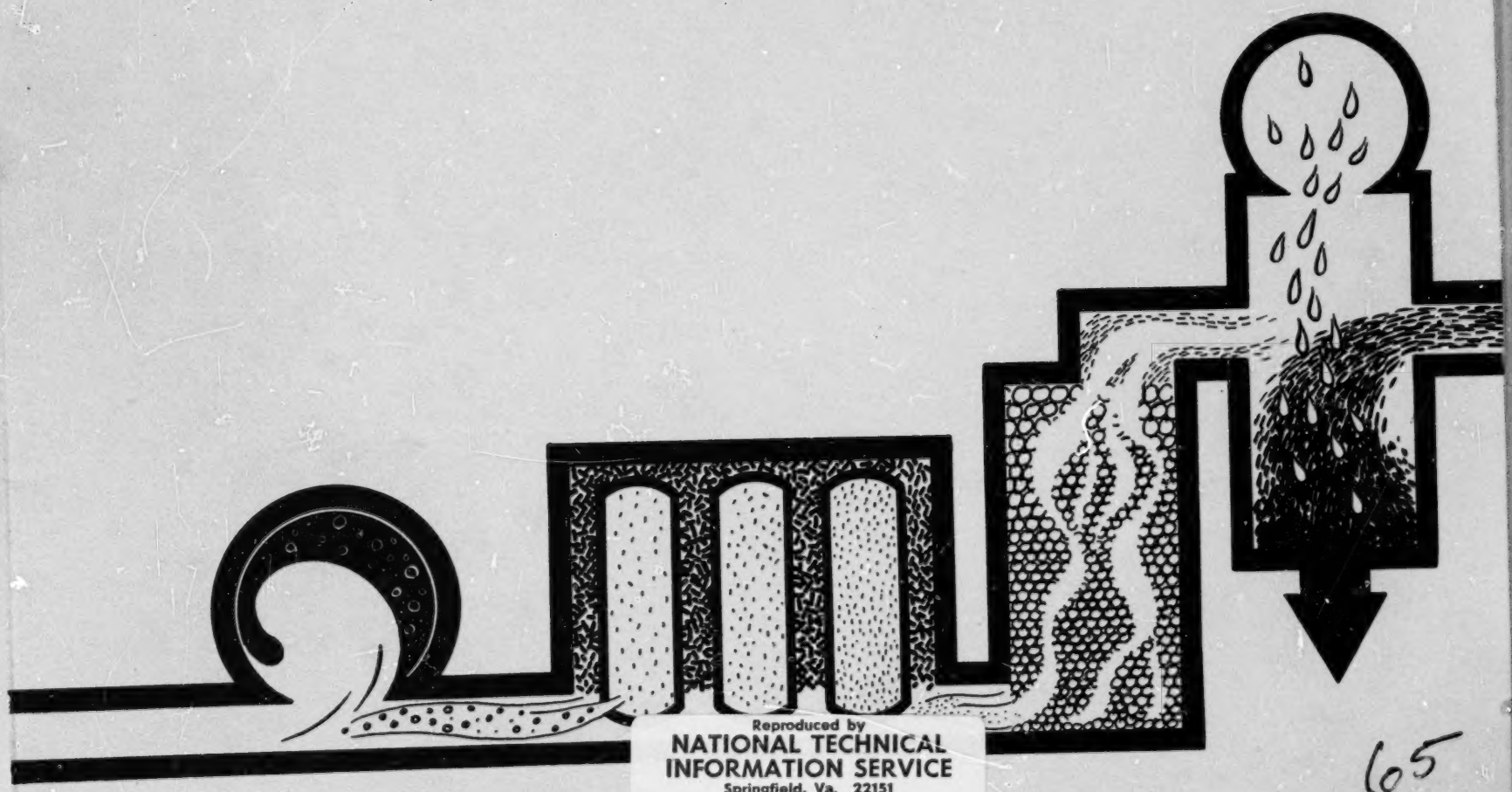
CLEAN WATER

WATER POLLUTION CONTROL RESEARCH SERIES ● 17040EUN02/71

W72 03782

PB 206 191

DEMINERALIZATION OF WASTEWATER BY THE TRANSPORT-DEPLETION PROCESS



Reproduced by
NATIONAL TECHNICAL
INFORMATION SERVICE
Springfield, Va. 22151

65

U. S. ENVIRONMENTAL PROTECTION AGENCY

1 Accession Number	2 Subject Field & Group	SELECTED WATER RESOURCES ABSTRACTS INPUT TRANSACTION FORM
W72-03782	05D, 03A	

5 Organization

Southern Research Institute
Birmingham, Alabama

6 Title

DEMINERALIZATION OF WASTEWATER BY THE TRANSPORT-DEPLETION PROCESS

10 Author(s)

Lacey, Robert E., and
Huffman, Everett L.

16 Project Designation

FWQA Contract Nos. 14-12-443 and 14-12-812

21 Note

Copy available from GPO Sup Doc as , $6.65; microfiche from NTIS as PB 206 191, $0.95.

22 Citation

Environmental Protection Agency) 17040 EUN,
Final report, ~~to Water Quality Office under Contract Nos. 14-12-443 and 14-12-812,~~ February, 1971.
86 p, 9 tab, 9 fig, 5 ref.

23 Descriptors (Starred First)

*Desalination processes, *Transport depletion, *Wastewater treatment
*Electrodialysis, Demineralization, Membrane processes, Sewage effluents, Municipal wastes,
Cost analysis

25 Identifiers (Starred First)

27 Abstract

The transport-depletion process was investigated for demineralizing municipal secondary effluent. Wastewater containing 850 mg/l. total dissolved solids and having a turbidity of 1 to 10 JTU, was demineralized continuously for 500 hours in a pilot plant at a rate of 3800 gpd.

Although regenerated-cellulose membranes were found to be satisfactory in regard to physical durability, the coulomb efficiencies attained with these membranes were only 0.14 to 0.28. The major problems encountered in demineralization of wastewaters by conventional electrodialysis, fouling and scaling, were, however, largely overcome by the use of a special anion-selective membrane and periodic flushing of the stack with sodium chloride solution. With the special anion-selective membrane, current densities up to three times the conventional limiting current density could be used without precipitation of pH-sensitive salts and coulomb efficiencies of 0.70 were obtained during the 500 hours of operation.

Membrane fouling, which caused the electrical resistance of the demineralizer stack to increase, was largely overcome by flushing the stack with a sodium chloride solution. This flushing technique should be useful for cleaning conventional electrodialysis stacks.

Cost estimates for a 10 mgd plant indicated a demineralization cost of 25.7¢/kgal for transport depletion compared to 27.8¢/kgal for electrodialysis and required activated-carbon pretreatment. The estimated cost for transport depletion is slightly lower because it does not require activated-carbon pretreatment.

~~This report was submitted in fulfillment of Contract Nos. 14-12-443 and 14-12-812 under the sponsorship of the Water Quality Office of the Environmental Protective Agency.~~
(EPA abstract)

Abstractor	Institution
Everett L. Huffman	Southern Research Institute, Birmingham, Alabama

WR:102 (REV. JULY 1969)
WRSIC

SEND TO: WATER RESOURCES SCIENTIFIC INFORMATION CENTER
U.S. DEPARTMENT OF THE INTERIOR
WASHINGTON, D. C. 20240

GPO: 1969-359-339

WATER POLLUTION CONTROL RESEARCH SERIES

The Water Pollution Control Research Series describes the results and progress in the control and abatement of pollution in our Nation's waters. They provide a central source of information on the research, development, and demonstration activities in the Environmental Protection Agency, through inhouse research and grants and contracts with Federal, State, and local agencies, research institutions, and industrial organizations.

Inquiries pertaining to Water Pollution Control Research Reports should be directed to the Head, Publications Branch, Research Information Division, R&M, Environmental Protection Agency, Washington, D. C. 20460.

DEMINERALIZATION OF WASTEWATER BY THE TRANSPORT-DEPLETION PROCESS

by

Southern Research Institute
Birmingham, Alabama 35205

for the

ENVIRONMENTAL PROTECTION AGENCY

Project #17040 EUN
Contract #14-12-812

February 1971

For sale by the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402 - Price 65 cents

EPA Review Notice

This report has been reviewed by the Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

ABSTRACT

The transport-depletion process was investigated for demineralizing clarified or filtered municipal secondary effluent. Wastewater containing 850 mg/l. total dissolved solids and having a turbidity of 1 to 10 JTU, was demineralized continuously for up to 500 hours in a pilot plant operating at a rate of 3,800 gpd.

Although regenerated-cellulose membranes, generally regarded as neutral membranes, were found to be satisfactory in regard to physical durability, the coulomb efficiencies attained with these membranes were only 0.14 to 0.28. The major problems encountered in demineralization of wastewaters by conventional electrodialysis, fouling and scaling, were, however, largely overcome by the use of a special anion-selective membrane and periodic flushing of the stack with sodium chloride solution. With the special anion-selective membrane, current densities up to three times the conventional limiting current density could be used without precipitation of pH-sensitive salts and coulomb efficiencies of 0.70 were obtained.

Membrane fouling, which caused the electrical resistance of the demineralizer stack to increase, was largely overcome by flushing the stack with a sodium chloride solution. This flushing technique should be useful for cleaning conventional electrodialysis stacks.

Cost estimates for a 10 mgd plant indicated a demineralization cost of 25.7¢/kgal for a system containing the special anion membrane compared to 27.8¢/kgal for the combination of conventional electrodialysis and required activated-carbon pretreatment. The estimated cost for the special membrane system is slightly lower because it does not require the activated-carbon pretreatment.

This report was submitted in fulfillment of Project Number 17040 EUN, Contract 14-12-812, under the sponsorship of the Water Quality Office of the Environmental Protection Agency.

CONTENTS

	Page
CONCLUSIONS	1
RECOMMENDATIONS	3
INTRODUCTION	5
PILOT-PLANT EQUIPMENT AND OPERATION	9
Equipment and Operation	9
Pretreatment of secondary effluent	9
Demineralizer Stack	16
Power Supply	17
Instrumentation	17
Typical Operating Procedure	17
MEMBRANES	19
Procedures for Evaluating Membranes	19
Transference number	20
Electrical resistance	20
Thickness	20
Electrolyte diffusion rate	20
Water permeability	21
Membrane Properties	21
Stability of Regenerated-Cellulose Membranes	23
RESULTS AND DISCUSSION	27
Chronology of Demineralization Runs	27
Membrane Fouling	31
Effect of fouling on cell-pair resistance	32
Effect of membrane fouling on coulomb efficiency	34
Treatments to Remove Fouling	34
Coulomb Efficiency	42
Neutral membranes	42
Ionac IM-12 anion-selective membranes	43
Alum Pretreatment of Wastewater	45
Effect of Removing Spacer Screens from Depleting Compartments	46
Effect of Solution Velocity and Product:Waste Ratio	47
Ion-Removal Selectivity	48
ECONOMIC CONSIDERATIONS	51
ACKNOWLEDGMENTS	57
REFERENCES	59

FIGURES

NO.		PAGE
1	DIAGRAM OF A TRANSPORT-DEPLETION STACK	7
2	TRANSPORT-DEPLETION PILOT PLANT (IN TRUCK TRAILER) AT THE SHADES VALLEY SEWAGE TREATMENT PLANT OF JEFFERSON COUNTY	10
3	TRANSPORT-DEPLETION STACK AND CONTROL PANEL	11
4	FLOW DIAGRAM OF TRANSPORT-DEPLETION PILOT PLANT	12
5	LOCATION OF MAJOR ITEMS IN THE TRANSPORT-DEPLETION TRAILER-MOUNTED PILOT PLANT	13
6	CHANGES IN CELL-PAIR RESISTANCE DURING TYPICAL OPERATION	33
7	CELL-PAIR RESISTANCE AND FEED TURBIDITY IN RUNS 97-105	39
8	CELL-PAIR RESISTANCE AND FEED TURBIDITY IN RUNS 106-114	40
9	CELL-PAIR RESISTANCE AND FEED TURBIDITY IN RUNS 115-122	41

TABLES

No.		Page
1	Analysis of Wastewater from Shades Valley Sewage Treatment Plant	14
2	Composition of Typical Feed Solution Used in Pilot Plant	15
3	Properties of Membranes	22
4	Decrease in Burst Strengths of Regenerated-Cellulose Membranes Exposed to Various Types of Water	25
5	Conditions and Results for Demineralization Runs 97-122	38
6	Conditions for and Results of Demineralization Runs 94-96	47
7	Ion-Removal Selectivity	49
8	Capital Costs for 10 mgd Demineralization Plant	53
9	Operating Costs for Demineralizing 10 mgd of Secondary Wastewater	55

CONCLUSIONS

This report includes work performed from June 28, 1968 to December 22, 1970, under Contracts 14-12-443 and 14-12-812.

The main conclusions are:

- A process which uses cation-selective membranes combined with special anion-selective membranes (IM-12 membranes from Ionac Chemical Company)* appears to be technically feasible for long-term demineralization of secondary sewage effluents if the stack is cleaned periodically by flushing with an 18% sodium chloride solution.

- The estimated total cost for demineralizing secondary effluents by the above process is slightly less than the cost of demineralization by conventional electrodialysis combined with activated-carbon pretreatment (estimated on the same basis).

Other conclusions are:

- Neutral membranes made of regenerated cellulose retain essentially all of their burst strength after 3 months service in the stack, however, the coulomb efficiencies with these membranes were only 0.14 to 0.28, which makes their use economically unattractive for demineralization.

- The special anion-selective membrane, Ionac IM-12, was useable with current densities up to three times the conventional limiting current density without encountering the usual precipitation of pH-sensitive salts. Coulomb efficiencies of

---

*Mention of proprietary equipment or products is for information only and does not constitute endorsement by the Environmental Protection Agency.

about 0.70 were obtained with this membrane when demineralizing wastewater in a long-term operation of more than 500 hours.

- Removing the spacer screens from the depleting compartments of the stack did not improve the effectiveness of removing the materials that caused fouling.

- Variations in solution velocity from 5 to 14 cm/sec and in product:waste ratio from 5:1 to 15:1 had no significant effects on cell-pair resistance or coulomb efficiency.

- Bicarbonate and calcium ions were removed to a greater degree than were other ions.

RECOMMENDATIONS

It is recommended that the IM-12 membranes and the sodium chloride cleaning technique be considered for use in various electromembrane processes for demineralizing secondary sewage effluents.

BLANK PAGE

INTRODUCTION

Use of the conventional electrodialysis process for demineralization of secondary sewage effluents, while promising, presents a number of operating problems. Major problems are temporary fouling of membranes by colloidal organic materials, permanent fouling of anion-selective membranes by both colloidal and dissolved organic materials in the feed, and scaling at the anion-selective membranes because of precipitation of pH-sensitive compounds. Brunner[1] found that the first two problems could be minimized by removing essentially all of the organic material from the wastewater by clarifying it and treating it with activated carbon. More recent work at the Pomona, California Advanced Waste Treatment Facility showed that granular carbon treatment of effluent from a well-operated secondary plant was sufficient for operation of electrodialysis. The cost of the activated-carbon treatment, however, is significant. The transport-depletion process is a variant of electrodialysis that offered promise for solving some of the problems encountered with electrodialysis without the necessity of activated carbon pretreatment.

The transport-depletion process is similar to conventional electrodialysis in that it removes soluble salts from water by passage of electric current through an array of ion-permeable membranes and thin solution compartments. The term "transport depletion" could properly be applied to all electromembrane processes, because their common basis for demineralization is the depletion (or enrichment) that occurs because of the transport of ions across ion-exchange membranes. However, the name "transport depletion" generally has been used to designate the electromembrane process in which near-neutral and cation-selective membranes are used, in contrast to conventional electrodialysis in which highly anion-selective and cation-selective membranes are used.

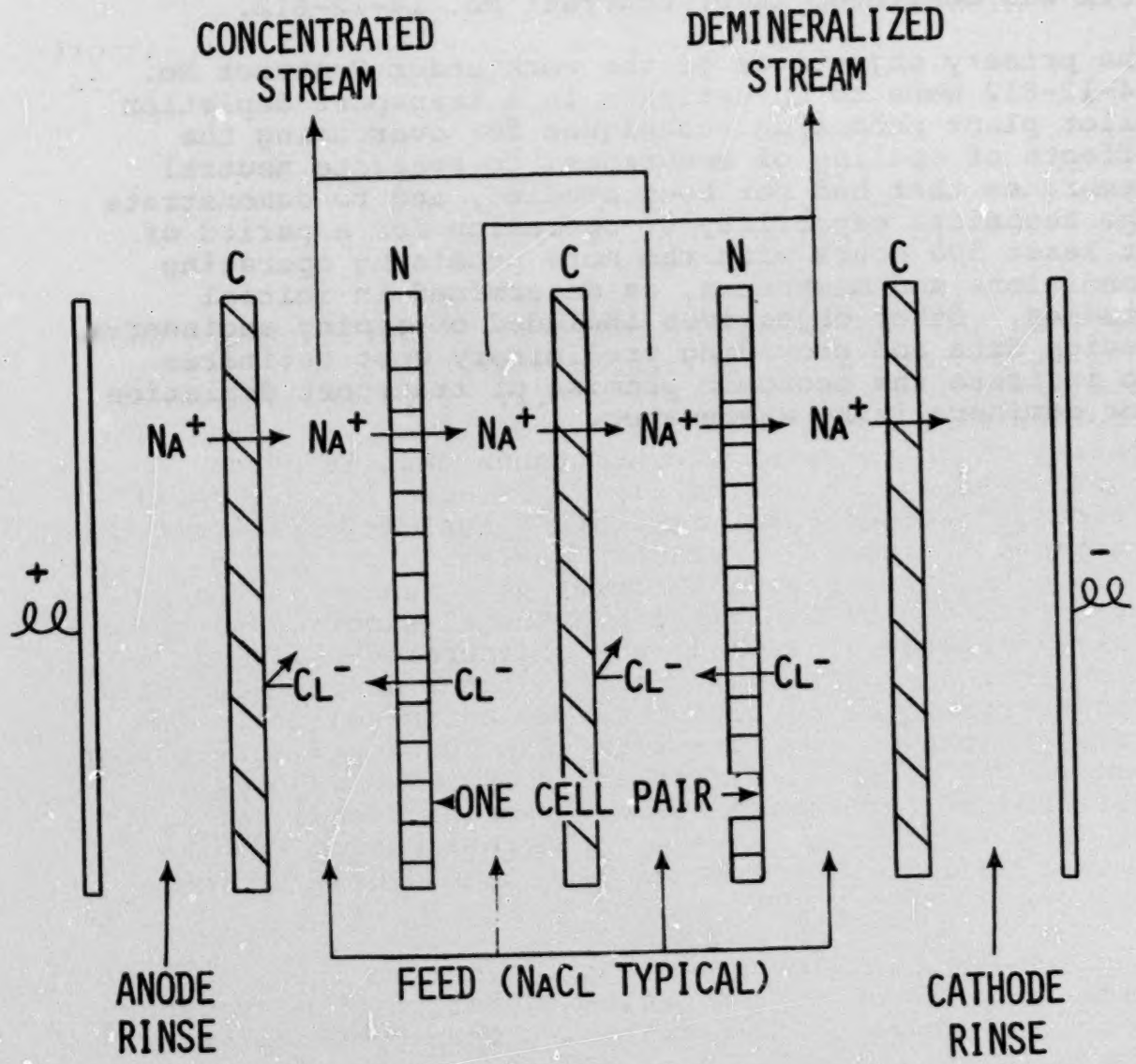
Even though we used a highly specialized type of anion-selective membrane in this program as well as near-neutral membranes, we have referred to both processes as transport depletion in this report.

Preceding page blank

A diagram of a transport-depletion stack is shown in Figure 1. The alternating cation-selective and neutral membranes cause the solution in every other compartment to become less concentrated in ions and that in the other compartments to become more concentrated in ions when direct electric current is passed through the stack. When direct electric current is passed through a transport-depletion assembly, depleted and enriched boundary layers form at the opposite sides of the cation-selective membranes, but there is no such effect at the nonselective neutral membranes. The neutral membranes serve only to separate the depleted and enriched streams from each other and, in doing so, they create alternating depleting and enriching compartments.

Previous studies at Southern Research Institute had shown that transport depletion offered several advantages for demineralizing waters that normally cause operating problems when conventional electrodialysis is used. The scaling of anion-selective membranes that is often encountered when electrodialysis is used for demineralization is avoided since no conventional anion-selective membranes are used. Transport depletion permits the use of much higher current densities and greater throughput rates than can be used in conventional electrodialysis. Neutral membranes, such as the regenerated-cellulose films that are ordinarily used in the transport-depletion process are lower in cost than the anion-selective membranes that they replace—less than $0.04 per square foot compared to $1 to $3 per square foot. The major disadvantage of the transport-depletion process is that it requires substantially more electrical energy for the removal of a given amount of salt than does electrodialysis.

Southern Research Institute carried out an initial feasibility study of the demineralization of wastewater (secondary sewage effluent) by the transport-depletion process under Contract No. 14-12-443. The primary objectives of the work were to determine on a pilot-plant scale the technical feasibility of the transport-depletion process for reducing the dissolved solids of secondary effluent and to determine whether the transport-depletion process could overcome the problems encountered when conventional electrodialysis is used to treat wastewater. The results obtained under Contract No. 14-12-443



C CATION-SELECTIVE MEMBRANE
N NEUTRAL MEMBRANE

Figure 1. Diagram of a Transport-Depletion Stack

indicated that the transport-depletion process had potential for demineralizing wastewater at a lower cost than electrodialysis if certain problems could be solved. A summary report covering the work under Contract No. 14-12-443 was prepared but not published because the work was continued under Contract No. 14-12-812.

The primary objectives of the work under Contract No. 14-12-812 were to investigate in a transport-depletion pilot plant promising techniques for overcoming the effects of fouling of membranes, to evaluate neutral membranes that had not been studied, and to demonstrate the technical capability of operation for a period of at least 500 hours with the more promising operating conditions and membranes, as determined in initial studies. Other objectives included obtaining engineer-design data and providing preliminary cost estimates to indicate the economic promise of transport.depletion for demineralizing wastewater.

PILOT-PLANT EQUIPMENT AND OPERATION

A mobile pilot plant was constructed to allow us to carry out on-site studies of the treatment of secondary effluent from a sewage plant. The site chosen was the Shades Valley Sewage Plant in the southwest part of Jefferson County, Alabama. This sewage-treatment plant, built in 1960, uses the activated-sludge process for secondary treatment of sewage and has a design capacity of 10 mgd. Under normal conditions, the flow rate varies from 5 to 8 mgd. In periods of heavy rainfall, infiltration into the sewerage system increases the maximum flow rate to 15 mgd. The Shades Valley plant treats domestic sewage and a small amount of industrial sewage from the southern part of the Birmingham metropolitan area. The industrial sewage sometimes includes some plating wastes that contain cyanide ions and metal ions, such as iron, zinc, cadmium, copper, and chromium.

Equipment and Operation

The transport-depletion pilot plant was installed in a truck van trailer, 32 feet long with standard rear doors and a 42-in. side door. Figures 2 and 3 are photographs of the trailer and the transport-depletion stack and control panel in the trailer, respectively. A flow diagram of the pilot plant is shown in Figure 4. The location of major items of equipment in the trailer is shown in Figure 5. The pilot plant was designed to operate continuously with minimal attention.

Pretreatment of secondary effluent

Analyses of samples of the wastewater effluent from the Shades Valley plant taken at 2-hour intervals over a 24-hour period gave the results shown in Table I. During this period, the plant flow rate ranged from 5.5 to 9.6 mgd.

The total concentration of ions in the Shades Valley wastewater was lower than in typical wastewater, which normally contains 700 to 850 mg/l. Therefore, concentrated solutions of calcium chloride, sodium sulfate, and sodium bicarbonate were metered into the wastewater to augment the dissolved solids content so that the feed water used in our studies contained about the same concentrations of ions as an average secondary effluent.

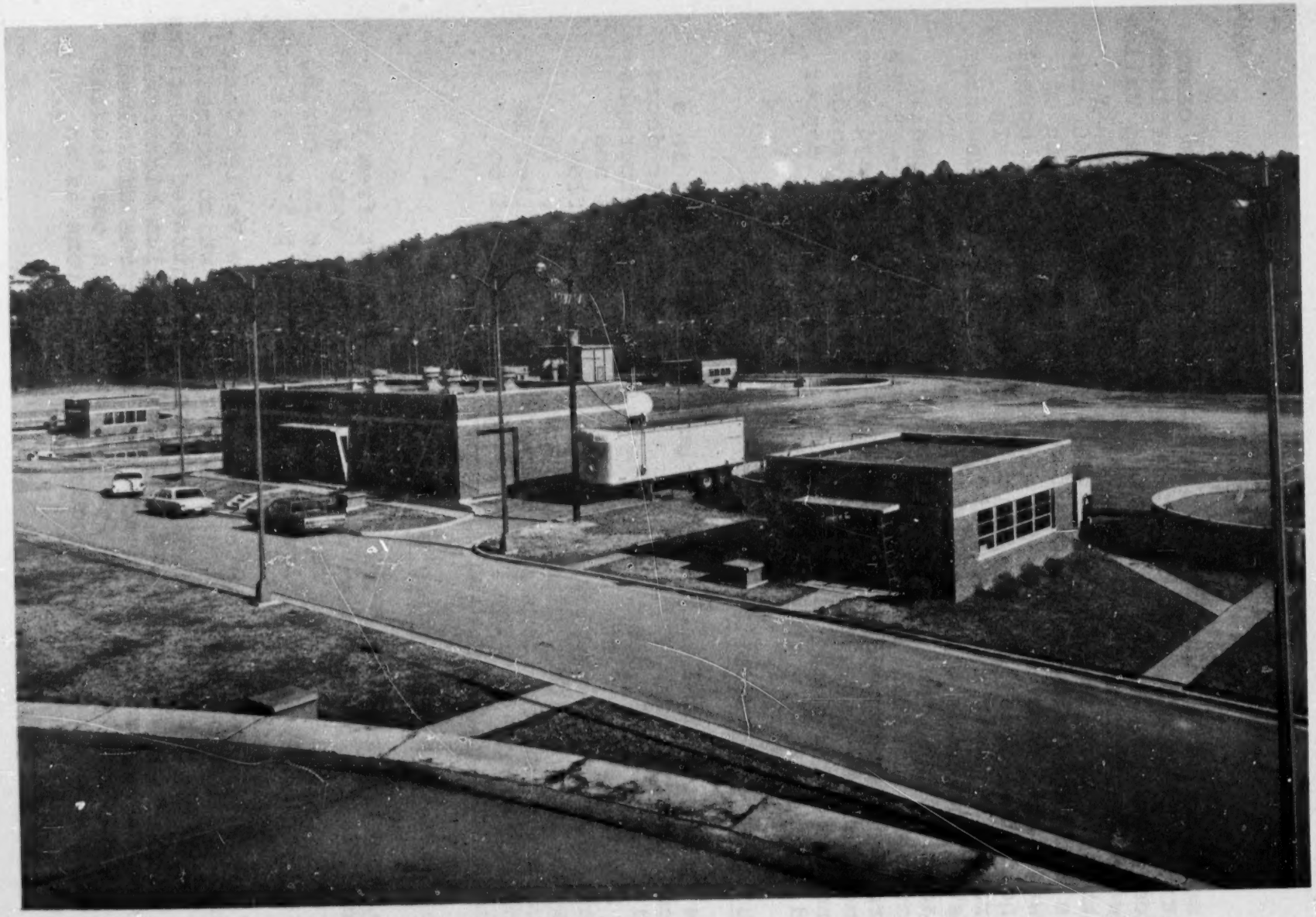


Figure 2. Transport-Depletion Pilot Plant (in truck trailer) at the Shades Valley Sewage Treatment Plant of Jefferson County

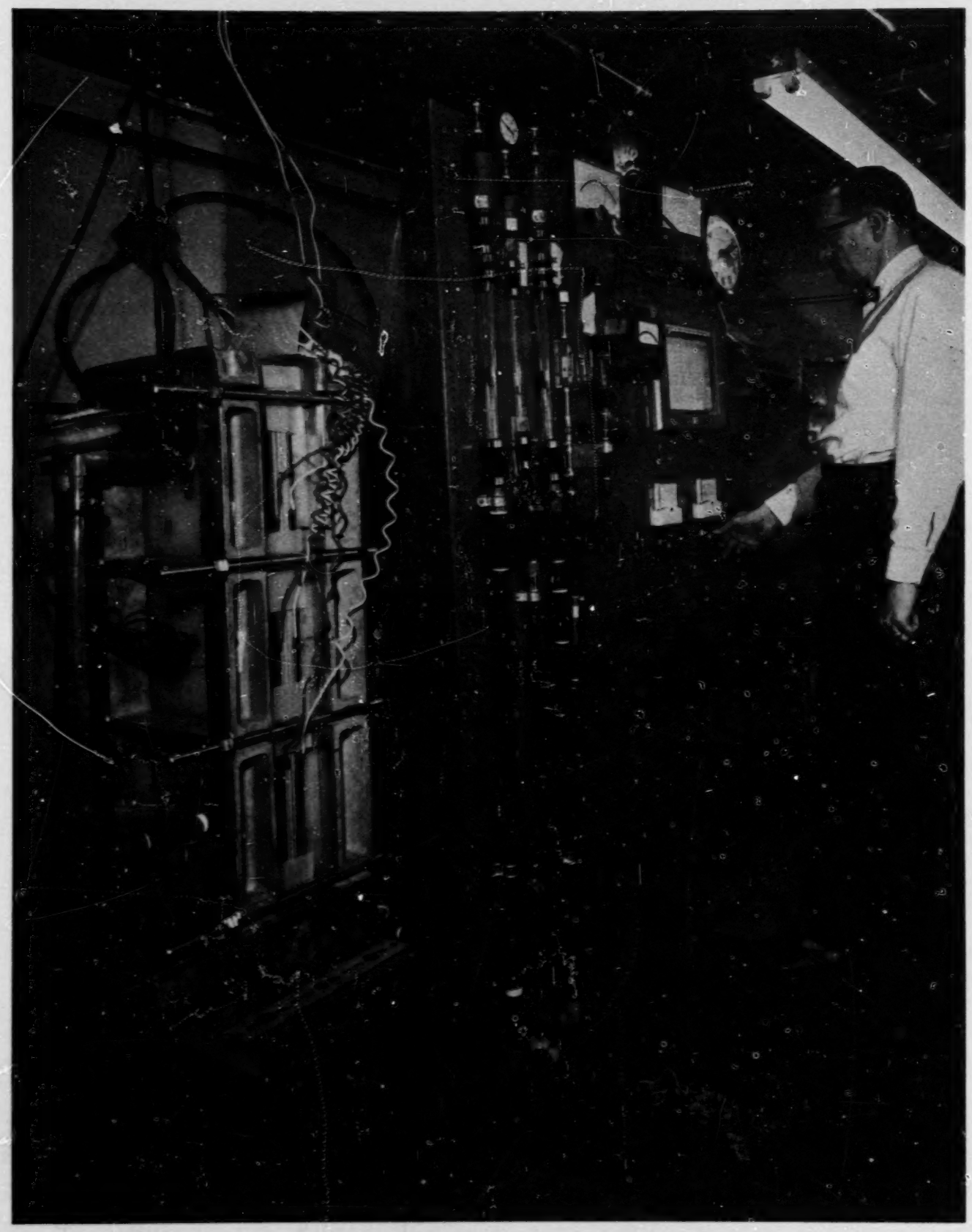


Figure 3. Transport-Depletion Stack and Control Panel

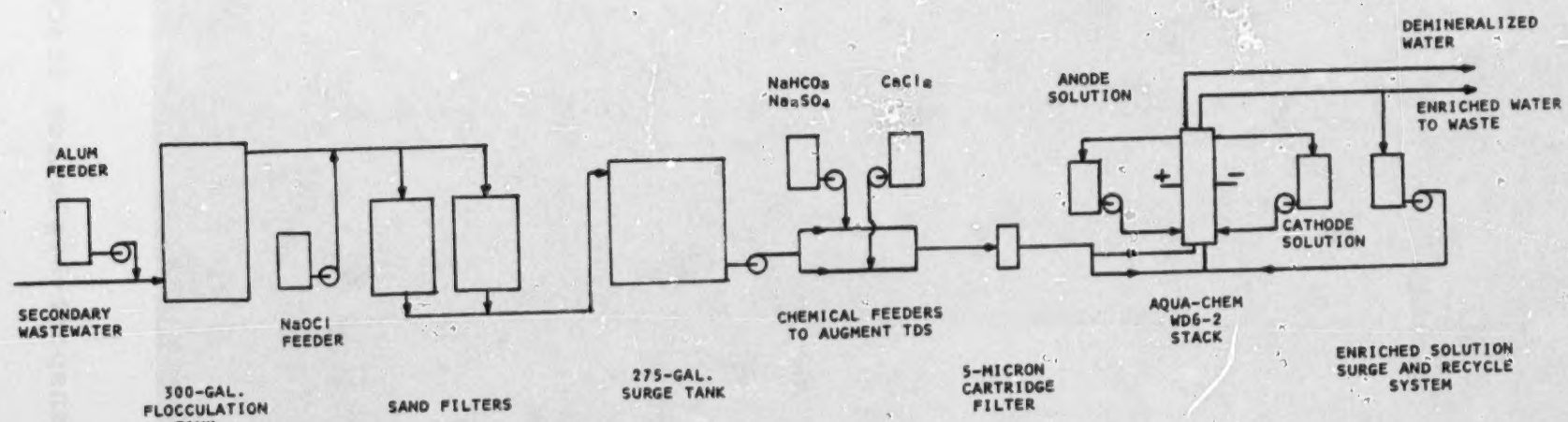
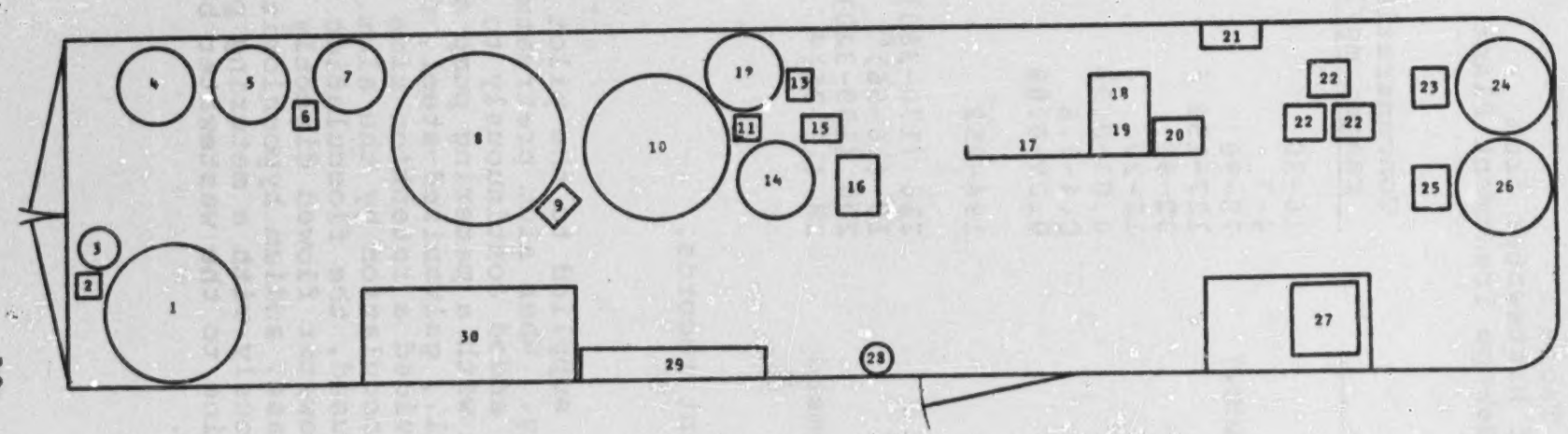


Figure 4. Flow Diagram of Transport-Depletion Pilot Plant



1. FLOCCULATION TANK
2. ALUM METERING PUMP
3. ALUM FEED TANK
4. SAND FILTER
5. SAND FILTER
6. SODIUM HYPOCHLORITE METERING PUMP
7. SODIUM HYPOCHLORITE FEED TANK
8. SURGE TANK
9. FEED PUMP
10. SODIUM SALTS FEED TANK
11. SODIUM SALTS METERING PUMP
12. CALCIUM CHLORIDE FEED TANK
13. CALCIUM CHLORIDE METERING PUMP
14. ENRICHED-RECYCLE TANK
15. ENRICHED-RECYCLE PUMP
16. DEMINERALIZER STACK
17. CONTROL PANEL
18. 12-POINT RECORDER
19. STACK POWER SUPPLY
20. pH METER
21. MAIN CIRCUIT BREAKER PANEL
22. ISOLATION TRANSFORMERS
23. ANOLYTE PUMP
24. ANOLYTE FEED TANK
25. CATHOLYTE PUMP
26. CATHOLYTE FEED TANK
27. SINK
28. NITROGEN CYLINDER
29. STORAGE SHELVES
30. WORK BENCH

Figure 5. Location of Major Items in the Transport-Depletion Trailer-Mounted Pilot Plant

Table I
Analysis of Wastewater from
Shades Valley Sewage Treatment Plant

Component	Concentration range, mg/l.
Calcium	16-30
Magnesium	4-7
Total hardness (as $CaCO_3$)	78-90
Bicarbonate	127-152
Sulfate	32-42
Chloride	15-20
Iron	0.03-0.34
Manganese	0.4-0.6
Chromate	0.05-0.08
Total ions	194-252
Total solids	216 (170-380)[a]
Suspended solids	16 (16-56)[a]
Dissolved solids	200 (150-320)[a]
Biochemical oxygen demand	28 (17-36)[a]

a. Shades Valley plant records.

The secondary effluent was supplied to the pilot plant at a pressure of about 65 psig. When alum pretreatment was used, an alum solution was added continuously to the incoming wastewater stream with a metering pump as the water flowed into a 300-gal., galvanized-steel, flocculation tank. The tank provided a retention time of 35-90 minutes to permit flocculation by the alum. When alum pretreatment was not used, the flocculation tank was by-passed and the wastewater flowed directly to the sand filters. In either case, sodium hypochlorite solution was added continuously with a metering pump to add about 5 mg/l. of chlorine to the wastewater before it entered the sand filter.

Two sand filters were used in parallel. These were Aqua-Guard MSF-2048 filters with epoxy-lined steel tanks 20 in. in diameter. Each contained 31 in. of 0.7-mm anthracite supported by a shallow layer of 0.3-0.6-mm calcite, graded-size gravel, and a distributor plate. The filters could be used singly or in parallel. The flow rate through these filters did not exceed 2 gpm/ft^2 at the maximum feed rate used. The chlorinated and filtered wastewater flowed into a 275-gal. polyethylene surge tank at a rate that maintained a small overflow from the tank.

The wastewater was pumped from the surge tank and the flow was divided into two equal streams. A concentrated calcium chloride solution was added continuously with a metering pump to one stream and a solution of sodium sulfate and sodium bicarbonate was added to the other. Each stream flowed through a chamber with internal baffles to cause mixing. The two wastewater streams with the added salts were combined, and fed to the demineralizer stack. The composition of a typical feed solution is shown in Table 2.

Table 2.
Composition of Typical Feed Solution
Used in Pilot Plant

Component	Concentration, mg/l.
Calcium	121
Magnesium	7
Total hardness (as $CaCO_3$)	331
Sodium	112
Potassium	11
Ammonium	7
Bicarbonate	263
Chloride	173
Sulfate	111
Phosphate	11
Total ions	816
Total dissolved solids	850

As shown in Figure 4, part of the enriched stream was recirculated to the stack after the addition of makeup feed solution. This was done to make the solution velocities equal in the enriching and depleting compartments of the stack even though the amount of depleted solution from the stack was several times greater than the amount of enriched solution going to waste. This method of operation resulted in essentially equal pressures on both sides of each membrane and prevented membrane distortion and poor distribution of solutions within the stack. The flow rates of the recycled enriched stream and of the makeup feed solution were adjusted to give the desired ratio of demineralized product to enriched or waste stream.

Demineralizer Stack

The demineralizer stack was an Aqua-Chem WD6-2 with 8 x 23.6 in. (20 x 60 cm) membranes. The effective area of each membrane was 116 in.^{2} (750 cm^2). The stack was normally assembled with 10 cell pairs. Ionac Chemical Company MC-3470 cation-selective membranes were used throughout the entire pilot-plant program. During most of the study Union Carbide Corporation Zephyr Z neutral membranes (made of regenerated cellulose) and Ionac Chemical Company IM-12 special anion-selective membranes were evaluated in the pilot plant. The stack was assembled with alternating cation-selective and neutral or anion-selective membranes, with a cation-selective membrane adjacent to both electrode compartments. The cell separators were of the sheet-flow type, 0.040 in. (0.10 cm) thick, and served as perimeter gaskets and membrane spacers. The inner part of the cell separators consisted of 11-mesh plastic screen. The hydraulic pressure drop through the stack was about 3 psi when the superficial solution velocity was 10 cm/sec. A superficial solution velocity of 10 cm/sec resulted in a flow of 0.277 gpm (1050 ml/min) through each compartment.

Electrode compartments, 0.10 in. (0.25 cm) thick, separated the platinized-titanium anode and the 316 stainless steel cathode from the cell pairs in the stack.

A solution of sodium carbonate was recirculated from a 50-gal. polyethylene tank through the anode compartment to neutralize the hydrogen ions formed at the anode and to provide a highly conductive electrical path between the anode and the cell pairs. Similarly, a solution of acetic acid was recirculated through the cathode compartment to neutralize the hydroxyl ions formed at the cathode and to provide an electrical path between the cathode and the cell pairs. Acetic acid was selected for use in the cathode rinse solution because of its buffering capability.

Power Supply

The direct current for the stack was obtained by rectification of three-phase 230-volt alternating current from isolation transformers. The a-c input voltage to the three-phase full-wave rectifier bridge was controlled by a continuously adjustable autotransformer. The d-c power to the stack could be varied continuously from 0 to 380 volts, with a maximum current of 50 A. The isolation transformers were found to be necessary to prevent electrical interference with measurements of conductivity and pH.

Instrumentation

A Leeds and Northrup 12-point recorder was used to record primary data during pilot-plant operation. Data that were recorded continuously were: temperature of the feed and depleted (product) streams, conductivities of the feed and depleted streams, stack current, and d-c voltage applied to the stack.

Typical Operating Procedure

In typical operation of the pilot plant, the filtered, chlorinated wastewater flowed continuously into the surge tank at a rate sufficient to maintain a small overflow. The feed-control valve was adjusted to give the desired flow rate of feed solution to the depleting compartments of the stack. The flow rates of the recycled enriched solution and of the makeup feed solution were adjusted to provide the desired product-to-waste ratio and to give a flow rate into the enriching compartments that was the same as that into the depleting compartments. The metering pumps for the supplemental salt solutions were adjusted to give the desired concentrations of

salts in the feed solution to the stack. Conductivity readings were used as indications of the salt concentration in the feed solution. When Ionac IM-12 anion-selective membranes were used, the enriched stream was maintained at a pH of 2.5-3.5 by adding 1 N hydrochloric acid to the enriched-stream recycle tank with a metering pump.

The input voltage to the rectifier bridge was adjusted to provide the desired d-c current or voltage to the stack. Except for slow changes caused by fouling of the membranes, steady-state conditions were attained within 15 minutes after adjustments of voltage or flow rates.

Samples of the feed and depleted streams were taken periodically for determinations of TDS and concentrations of the principal ions. Turbidity measurements on the feed solution were made with a Hach Laboratory Turbidimeter, Model 2100. The sand filters were backwashed and the solutions for augmentation of TDS of the feed were replenished as needed without interrupting the continuous operation of the demineralizer stack.

MEMBRANES

The properties of various types of films were determined in an effort to find better neutral membranes. A truly neutral membrane is one in which the transference numbers of ions are the same as their transference numbers in solution, e.g., a cation transference number (t^+) of 0.39 in sodium chloride solutions. Other desirable characteristics of neutral membranes for the proposed use are low electrical resistance, good mechanical strength and stability, and low cost.

In prior work on the transport-depletion process,[2,3] more than 80 materials were evaluated at Southern Research Institute for possible use as neutral membranes. Films made of regenerated cellulose were found to have the most promising combinations of properties for use as neutral membranes. However, the transference numbers (t^+) of most of these materials were significantly higher than 0.39 in sodium chloride solutions, especially at the salt concentrations of about 0.015 N which are typical of wastewater.

The search for better neutral membranes was continued in work under the present contract. Eight potential neutral membrane materials that were not available for our earlier studies were evaluated. None of the near-neutral membranes investigated were found to have a completely satisfactory combination of properties. As a result we investigated the Ionac Chemical Company IM-12 anion-selective membrane material. Ionac IM-12 is a special type of anion-selective material that is relatively porous and permits hydrogen ions to pass through it at a greater rate than through conventional anion-exchange membranes. These characteristics reduce the tendency of the membranes to become fouled or scaled compared to conventional anion-exchange membranes.

Procedures for Evaluating Membranes

Where possible, the methods given in the Office of Saline Water Test Manual[4] were used for the evaluation of membranes. Other test methods were developed when required.

Transference number

The procedure used to determine the transference number of a membrane was similar to Method 602.1 in the Office of Saline Water Test Manual. A membrane specimen was mounted in a concentration cell so that it separated two sodium chloride solutions of different concentrations. Each solution flowed through the cell at a rate of 1 l./min to maintain constant salt concentrations and to minimize polarization effects. The potential between silver-silver chloride electrodes in the two sodium chloride solutions was measured with a potentiometer. The transference number, t^+, was calculated by dividing the measured potential by the theoretical potential for the two sodium chloride concentrations.

Electrical resistance

The a-c electrical resistance of membranes was determined by a procedure similar to Method 601.1 in the Office of Saline Water Test Manual. A membrane specimen was clamped between two identical half-cells, each containing a platinized platinum electrode. Sodium chloride solutions of the same concentration flowed through each half-cell. The resistance between the electrodes was measured with the membrane specimen in place and again after it had been removed. The membrane resistance was calculated from the difference in the resistance of the cell with and without the membrane and the area of membrane exposed to the solution.

Thickness

The thickness of a wet membrane was measured at a minimum of five locations with a Randall and Stickney dial micrometer having a 6 DW weight and a pressure foot 0.75 in. in diameter.

Electrolyte diffusion rate

The procedure for determining the electrolyte diffusion rate consisted of clamping a membrane specimen between two compartments of a Plexiglas cell and adding 1.5 N sodium chloride solution to one compartment and a measured amount of deionized water to the other. The contents of both compartments were stirred. The concentration of sodium chloride in the compartment that

initially contained deionized water was determined by conductivity measurements at 10-min intervals for 1 hr. From these data, the electrolyte diffusion rate was calculated as the equivalents of sodium chloride diffused per square centimeter of membrane per hour and the membrane diffusion coefficient was calculated from the electrolyte diffusion rate and the membrane thickness.

Water permeability

The water permeability of a membrane was determined by placing a membrane specimen in a pressure-filter apparatus with water on top of the specimen and applying pressure to the water. The rate of water transfer through the membrane was measured and the water permeability, in ml/min-cm^2-psi, was calculated.

Membrane Properties

The properties of the various membranes that were evaluated in this program for use in the transport-depletion process are given in Table 3.

All of the neutral membranes shown in Table 3 had at least one property which made them less than ideal for use as membranes in the transport-depletion process. The transference numbers, t^+, of most of the membranes were significantly higher than the desired value of 0.39 at the salt concentration typical of wastewater (about 0.015 N).

The properties of the small sample of Yumicron Y-101 membrane obtained originally indicated that this material should be evaluated as a neutral membrane in the pilot plant. However, when Y-101 membranes from a new lot were installed in the stack, leakage between the enriching and depleting compartments was excessive, and the water permeability of the new membranes was found to be 0.26 ml/min-cm^2-psi, compared to a value of 0.03 ml/min-cm^2-psi for the original sample. The supplier replaced the Y-101 membranes with Y-601 membranes, but these were not suitable for use because of the high t^+ value (0.71).

The Yumicron Y-121, Y-203, and Y-621 membranes were dropped from consideration because of their high permeabilities to water. The Yumicron Y-201 membrane was dropped from consideration because of its extremely high electrical resistance.

Table 3
Properties of Membranes

Membrane designation	Transference number,[a] t^+ 0.1 vs 0.2 N NaCl	0.01 vs 0.02 N NaCl	0.005 vs 0.01 N NaCl	Electrical resistance, a-c, in 0.05 N NaCl, ohm cm^2	Electrolyte diffusion rate,[b] eq/cm^2-hr	Thickness, wet, cm	Membrane diffusion coefficient, cm^2/sec	Water permeability ml/min-cm^2-psi
Neutral membranes								
Yumicron[c] Y-101[d]	0.41	0.52	0.57	6	161×10^{-5}	0.010	287×10^{-6}	0.03
Yumicron[c] Y-101[e]	-	-	-	-	-	-	-	0.26
Yumicron[c] Y-121	0.42[k]	0.56	0.60	12	-	-	-	5.1
Yumicron[c] Y-202	0.36[k]	-	0.58[k]	39,000	-	-	-	0
Yumicron[c] Y-203	0.40	0.48	0.51	4	231×10^{-5}	0.006	274×10^{-6}	0.14
Yumicron[c] Y-601	-	0.71	-	26	83×10^{-5}	0.009	134×10^{-6}	0.001
Yumicron[c] Y-621	0.40	0.50	0.55	10	-	-	-	5.4
Eastman[f] HT-00	0.37	-	0.37	4	171×10^{-5}	0.009	284×10^{-6}	0.001
Eastman[f] HF-35	0.38	-	0.40	6	132×10^{-5}	0.011	268×10^{-6}	0.001
UCC[g] Zephyr Z	0.41	0.58	0.70	15	70×10^{-5}	0.012	149×10^{-6}	0
AHT[h] 4465-A2-4.9	0.38	0.47	-	23	32×10^{-5}	0.021	-	-
Ion-exchange membranes								
Ionac IM-12[i]	0.04	0.02	0.04	12	14×10^{-5}	0.014	38×10^{-6}	0
Ionac MC-3470[j]	0.98	0.96	0.96	35	-	-	-	-

a. Determined from measurements of concentration potentials between the concentrations shown.
b. From 1.5 N NaCl solution to deionized water.
c. Yuasa Battery (America), Inc.
d. Original sample.
e. Lot installed in stack.
f. Eastman Chemical Products, Inc.
g. Union Carbide Corporation, regenerated cellulose casing.
h. Arthur H. Thomas Co. dialyzer tubing, 4465-A2-4.9.
i. Ionac Chemical Company, anion-selective.
j. Ionac Chemical Company, cation-selective.
k. Value is questionable because of extremely high resistance of membrane.

As shown in Table 3, all of the values for the Eastman HT-00 and HF-35 membranes were very good. However, satisfactory seals could not be obtained with either type of Eastman membrane in the pilot-plant stack. Although the stack clamping bolts were tightened to twice the normal torque, there was leakage of solution between the enriching and depleting compartments of the stack. Both of these Eastman membranes were thin and easily torn. Neither of these membranes is suitable for use in the Aqua-Chem WD6-2 stack.

The properties of the AHT 4465-A2-4.9 regenerated-cellulose membrane material that had been used in our prior work[2,3] on the transport-depletion process were slightly better than those of the Zephyr Z material. However the AHT material is not available in sufficient width for use in the Aqua-Chem WD6-2 stack.

Consideration of the properties of the neutral membranes listed indicated that the Union Carbide Corporation Zephyr Z regenerated-cellulose membrane was the best available neutral membrane for use in the pilot-plant studies. The Zephyr Z membrane was, therefore, used in the pilot-plant studies with neutral membranes.

The Ionac IM-12 anion-selective membrane was evaluated in the pilot plant because of its unique properties. The IM-12 membrane is relatively porous and permits hydrogen ions to pass through it at a greater rate than through conventional anion-exchange membranes. The manufacturer states that this porosity causes the IM-12 membrane to have less tendency to be fouled by organic and inorganic materials than conventional anion-exchange membranes.

The Ionac MC-3470 cation-exchange membrane was selected for use in the pilot-plant studies because of its very good physical and electrochemical properties. (Table 3)

Stability of Regenerated-Cellulose Membranes

Prior to this study, a question was raised regarding the ability of regenerated cellulose to withstand biological attack by the secondary effluent unless the wastewater were chlorinated before it entered the demineralizer stack. Also, metal ions, such as those from plating wastes, might promote oxidative degradation of the neutral membranes.

Specimens of the AHT 4465-A2-4.9 and UCC Zephyr Z membranes were placed in the final clarifiers of the Shades Valley and Patton's Creek sewage treatment plants, both of which are operated by Jefferson County. As mentioned earlier, the Shades Valley plant sometimes treats sewage containing metal plating wastes, but the Patton's Creek plant treats only domestic sewage. The Mullen burst strengths of the specimens were measured after 15 days of exposure to the wastewater. The results of these measurements, Experiments 1 and 2 in Table 4, showed that the burst strengths of the specimens of both membrane materials decreased by at least half in 15 days of exposure. There was no significant difference in the rates of degradation at the two plants, which indicates that the small amounts of metal ions from the plating wastes that are treated by the Shades Valley plant did not affect the physical stabilities of the membranes.

Studies of the effects of metal ions and chlorination on the degradation of the neutral membranes were made in our laboratory. Specimens of membranes were exposed to chlorinated and continuously aerated Birmingham tap water to which salts had been added to provide concentrations of 1 mg/l. of chromium, 1 mg/l. of copper, 1 mg/l. of iron, and 3 mg/l. of manganese. Chlorinated and aerated Birmingham tap water was used as a control. The results of Experiments 3 and 4 in Table 4 indicate that this water, with or without the addition of the metal ions, caused no significant loss in the burst strengths of the membranes.

Membrane specimens exposed to continuously aerated Shades Valley wastewater in the laboratory (Experiment 5) were degraded to about the same degree as those exposed at the plant. The purpose of Experiment 6 was to determine whether chlorination of the wastewater would reduce the rate of degradation of the neutral membranes. Since chlorine was added only once or twice each day, the residual chlorine concentration varied from 0 to 0.7 mg/l., and usually reached a value of zero overnight. The results indicate that this method of addition of chlorine was not effective in reducing the degradation of the regenerated-cellulose membranes. The experiment with chlorinated wastewater was repeated (Experiment 7) with continuous addition of chlorine to provide a residual chlorine level of 0.3 to 1 mg/l. After 8 weeks of exposure to this wastewater, the AHT 4465-A2-4.9 membrane retained 93% of its original burst strength and the UCC Zephyr Z membrane retained 86%.

Table 4

Decrease in Burst Strengths of Regenerated-Cellulose Membranes Exposed to Various Types of Water

Experiment	Type of water	Length of exposure, days	Decrease in burst strength, % AHT[a]	Decrease in burst strength, % Zephyr Z[b]
Plant clarifier exposures				
1	Shades Valley wastewater	15	59	63
2	Patton's Creek wastewater	15	50	76
Laboratory experiments				
3	B'ham tap water, aerated, chlorinated	14	0	0
4	B'ham tap water, aerated, chlorinated, with metal ions added[c]	14	1	4
5	Shades Valley wastewater, aerated,	14	47	76
6	Shades Valley wastewater, aerated, chlorinated intermittently	14	57	36
7	Shades Valley wastewater, aerated, chlorinated continuously	56	7	14
Used in demineralization stack				
-	Shades Valley wastewater, chlorinated	90	-	0

a. Arthur H. Thomas Co. dialyzer tubing, 4465-A2-4.9.

b. Union Carbide Corporation Zephyr casing, Z.

c. Water contained: 1 mg/l. of Cr, 1 mg/l. of Cu, 1 mg/l. of Fe, 3 mg/l. of Mn.

These results indicated that the neutral membranes could be expected to remain serviceable in transport-depletion stacks for periods of 2 months or more, if the wastewater feed to the demineralizer were chlorinated.

The UCC Zephyr Z membranes that were used in the demineralizer stack in the pilot plant exhibited excellent resistance to degradation. The membranes that were removed from the stack for burst tests had been in the stack for 3 months. For most of this period, the stack was filled with primary or secondary effluent containing 0.1 to 3.0 mg/l. of residual chlorine. The average Mullen burst strength of these membranes was 23 psi, which was the same as that found for control (unexposed) specimens taken from the same roll of regenerated-cellulose film. A second set of Zephyr Z membranes that was subjected to similar conditions in the stack for 2.5 months showed no evidence of degradation.

The excellent physical condition of the Zephyr Z membranes after 3 month's use in the demineralizer stack strongly suggests that these membranes would be useable for a much longer time.

RESULTS AND DISCUSSION

All results given in this report are from demineralization runs made with the stack containing ten cell pairs. In all runs, sodium hypochlorite was added to provide a residual chlorine content of 1-3 mg/l. in the feed solution to the stack. The runs are numbered in chronological order. After Run 25 a run number was assigned to each calendar day of pilot-plant operation. Letters after a hyphen in some run numbers indicate periods of operation with different conditions. Union Carbide Corporation Zephyr Z neutral membranes (made of regenerated cellulose) were used in Runs 1-39. Ionac Chemical Company IM-12 special anion-selective membranes were used in all subsequent pilot-plant runs.

Chronology of Demineralization Runs

Runs 1-10 were short runs (about 1 hour each) with secondary effluent to determine the effects of superficial solution velocities of 5, 10, and 15 cm/sec and current densities of 3.3 to 43.3 mA/cm^2 on demineralization performance. Membrane fouling was encountered in this series of runs, which limited the amount of reliable data that could be obtained on the effects of these two operating parameters.

Runs 11 and 12 were not typical of normal operation because the wastewater from the sewage treatment plant was essentially primary effluent that had been subjected to one additional stage of clarification. Because of heavy rainfall, infiltration of ground water into the sewerage system greatly diluted the raw sewage entering the plant, and secondary treatment was stopped to conserve fuel gas used for compressing air.

Runs 13-15 were made after the sewage treatment plant resumed normal secondary treatment. These runs were made without disassembling and cleaning the stack following Run 12. The secondary wastewater feed to the demineralizer was treated with alum to reduce the turbidity and the fouling of the membranes. However, the fouling that remained from Runs 11 and 12 severely hampered the operation of the pilot plant.

Runs 16-18 were made with alum-treated secondary wastewater after the stack had been disassembled and cleaned. The alum dosage was 35 to 50 mg/l., which laboratory jar tests showed was optimum for this water. Runs 16-18, lasting 7 to 11 hours each, were made on consecutive days with overnight shutdowns. Although membrane fouling caused the electrical resistance of the stack to increase, no operating difficulties were encountered in Runs 16-18.

Runs 19-25 were made over a period of 139 hours of almost continuous operation. The duration of the individual runs ranged from 5.5 to 32.7 hours. Before each run, one of several treatments to reduce the fouling on the membranes was tried.

When pilot-plant operations were resumed under Contract No. 14-12-812, Runs 26 and 27 were made to check the operability of the pilot plant with a sodium chloride feed solution. The stack and other pilot-plant equipment were found to be in good operating condition.

Runs 28-39 were made to determine the effectiveness of flushing the stack with short bursts of nitrogen for controlling the fouling of membranes. Nitrogen flushing was tried with the stack current off and with the polarity of the stack current reversed. The technique of nitrogen flushing with the polarity of the stack current reversed was more beneficial in reducing membrane fouling. However, it was not adequate to prevent substantial increases in stack resistance and decreases in coulomb efficiency over long periods of operation.

Ionac IM-12 anion-selective membranes were installed in the stack after Run 39 and were used in all subsequent pilot-plant runs. The results of Runs 40-42 with a sodium chloride feed solution showed that coulomb efficiencies 0.90 or higher were obtained with the IM-12 membranes.

Runs 43-55 were made to determine the effectiveness of cleaning the stack, and thus reducing the effects of membrane fouling, by circulating a solution of an enzyme-active laundry material through the stack at 12-hr intervals. However, the high pH of the calcium chloride solution used to increase the calcium concentration of the wastewater feed solution caused precipitation in the feed lines and in the depleting compartments of the

stack and caused the data from these runs to be unreliable. The high pH was caused by the use of a new lot of calcium chloride that was found to contain more than the usual amount of calcium hydroxide.

The purpose of Runs 56-65 was the same as for Runs 43-55. The results of Runs 56-65 indicated that circulation of a solution of an enzyme-active laundry material through the stack for 1 hr at 12-hr intervals was effective for cleaning the stack and reducing the cell-pair resistance.

Runs 66-70 were made to determine the effectiveness of a concentrated solution of sodium chloride in place of the solution of enzyme-active laundry material for cleaning the stack at 12-hr intervals. The results of Runs 66-70 indicated that a concentrated sodium chloride solution was more effective than the enzyme-active laundry material in cleaning the stack and reducing cell-pair resistance.

The purpose of Runs 71-74 was to determine the effect of variations in solution velocity and product:waste ratio on coulomb efficiency and cell-pair resistance. The erratic results obtained in Runs 71-74 indicated that the runs should be repeated before drawing conclusions about the effects of solution velocity and product:waste ratio on demineralization performance.

Runs 75-85 were made to determine whether alum treatment of the wastewater would significantly reduce the problems with fouling in the stack. During these runs the stack was flushed at 24-hr intervals with a sodium chloride solution. The results with alum-treated wastewater indicated that, although the use of alum reduced the turbidity of the feed solution to the stack, the cell-pair resistances before and after flushing with the sodium chloride cleaning solution were not significantly different from those obtained in runs with wastewater that had not been treated with alum.

Runs 86-89 were made to determine whether removing the spacer screens from the depleting compartments would facilitate the removal of the membrane-fouling material from the compartments by flushing. The results of the runs indicated that removing the spacer screens from the depleting compartments was not beneficial.

Runs 90-93 were made to determine the effect of solution velocity and product:waste ratio on demineralization performance. However, it was found that the Ionac IM-12 membranes in the stack were irreversibly fouled. After Run 93 the membranes in the stack were replaced with new Ionac MC-3470 cation-selective and Ionac IM-12 anion-selective membranes.

In Runs 94-96 it was determined that variations in solution velocity and product:waste ratio over the ranges investigated had no significant effects on coulomb efficiency or cell-pair resistance.

Runs 97-122 were made over a period of approximately 600 hours of continuous operation to determine the long-term operating characteristics of the process and to obtain operating data for use in estimating the costs of demineralization. During Runs 97-118 the stack was flushed with a sodium chloride solution at 24-hr intervals. During these runs, cleaning the stack with the sodium chloride solution was effective in restoring the coulomb efficiency and cell-pair resistance to near the original values. The data from Runs 97-118 indicated that the average cell-pair resistance* increased from about 1050 ohm cm^2 to about 1550 ohm cm^2 and remained at about this level although there were some changes with the turbidity of the feed. The average coulomb efficiency values were essentially constant at about 0.70 during the last 300 hr of this series.

During Runs 119-121 the long-term operation was continued with the same conditions except that the stack was flushed with tap water instead of the sodium chloride solution. The tap water was less effective than the sodium chloride solution in cleaning the stack and there was a significant decrease in coulomb efficiency during these runs.

---

*The time-average cell-pair resistance was calculated for each run.

In Run 122, flushing the stack with a sodium chloride solution was less effective in cleaning the stack than it had been in the runs before water was tried for flushing.

Membrane Fouling

Fouling of membranes or the effects of fouling were observed in most runs with wastewater, regardless of the operating conditions or the type of pretreatment used. Whenever the stack was opened for inspection a brown, flocculent, slightly slimy material was found to be fairly evenly distributed throughout each depleting compartment. When the stack was inspected after being flushed with solutions of an enzyme-active laundry material or of sodium chloride the amount of fouling material was small, but some was always present. The fouling material was found both in the mesh of the spacer screens and on the sides of both of the membranes facing the depleting compartments. Both the UCC Zephyr Z neutral membranes and the Ionac IM-12 anion-selective membranes became more heavily coated with the fouling material than the Ionac MC-3470 cation-selective membranes. Most of the flocculent fouling material could be removed easily by rinsing with water; a thin layer of finely divided material remained on the neutral and anion-exchange membranes, but this was easily removed by light rubbing. The enriching compartments contained only traces of the fouling material.

When the fouling material was heated in a flame, most of the material was consumed and only traces of ash remained, indicating that it was mostly organic material. Polishing filters with 5-micron cartridges collected only a small quantity of material and had no significant effect on the turbidity of the feed solution which indicates that the particle size of the material that caused fouling was less than 5 microns. Presumably, the material consisted mostly of negatively-charged particles of organic compounds or colloids that were too large to pass through the neutral or anion-selective membranes.

Effect of fouling on cell-pair resistance

The most important effect of the membrane fouling was an increase in the cell-pair resistance and an associated decrease in stack current for demineralization (when the stack voltage was held constant). The R_{cp} values in this report are normalized for a feed-solution temperature of 25°C and a log mean concentration of 675 mg/l. (0.01 $\underline{N}$) in the depleting compartments. The R_{cp} values were normalized to 25°C by applying the temperature coefficient for the resistance of the solution being demineralized. (Data reported by Casolo and Leitz[5] showed that the temperature coefficient of resistance for an electrodialysis stack was essentially the same as that for the solution in the stack.) The normalities of the solutions were calculated from the concentrations in mg/l. by use of the average equivalent weight of the salts in solution (67.5 g/eq), as determined from analyses of samples of feed and product (demineralized) water. Prior work[3] with the transport-depletion process showed that the product of cell-pair resistance and the log mean normality of the depleting solution, $R_{cp}\underline{N}$, is constant over the range of concentrations used in this program. Normalizing the cell-pair resistance values to a given mean concentration permits comparisons of cell-pair resistances with a given stack regardless of the feed concentration and the degree of demineralization.

The cell-pair resistance generally increased rapidly during the first 1 to 2 hr of operation after the membrane fouling had been removed and then continued to increase at a fairly constant, but much lower rate, for the duration of the run.

Figure 6 shows the change in cell-pair resistance during typical operation in the continuing series of runs.

There was no significant difference in the rates of fouling with UCC Zephyr Z neutral membranes or Ionac IM-12 anion-selective membranes.

Although no quantitative correlation was found between the turbidity of the feed solution and the rate of increase in cell-pair resistance (or rate of fouling), the cell-pair resistance did increase when the turbidity of the feed solution increased.

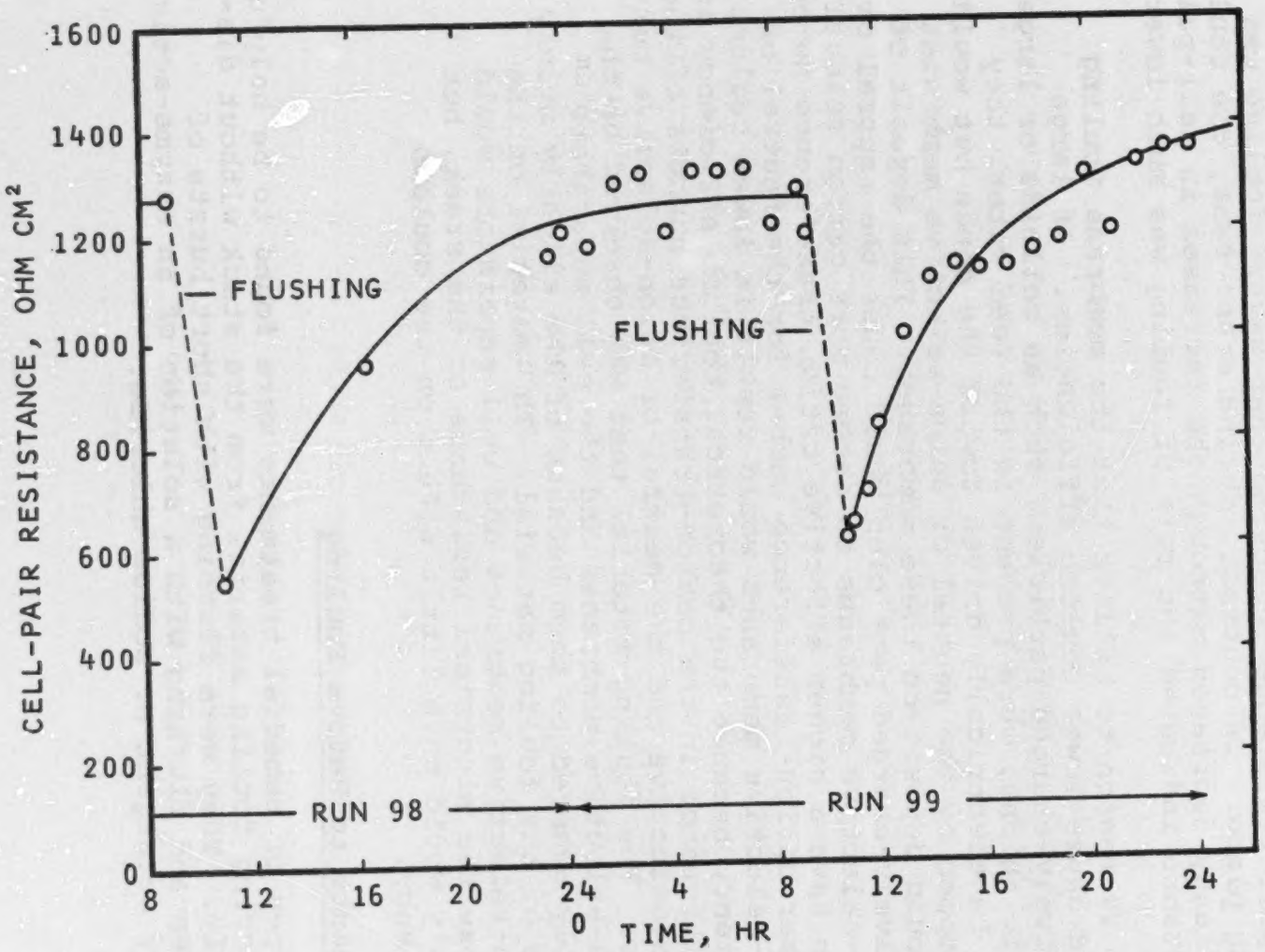


Figure 6. Changes in Cell-Pair Resistance During Typical Operation

Effect of membrane fouling on coulomb efficiency

The overall results of the demineralization runs indicate that membrane fouling generally caused some reduction in coulomb efficiency. However, correlation between coulomb efficiency and the degree or rate of membrane fouling was not good. For example, in some runs the coulomb efficiency increased or remained constant although the increases in cell-pair resistance indicated that severe fouling was taking place. In contrast, during other runs, the coulomb efficiency decreased although the increases in cell-pair resistance indicated the rate of fouling was much lower.

There is reason to believe that the membrane fouling should cause lower coulomb efficiencies. If large negatively-charged particles, such as colloids or large organic anions, were present in the feed water, they would be electrically driven toward the anode but would be stopped by the neutral or anion-selective membranes and would deposit on these membranes. This deposit of negatively-charged particles would cause the neutral or anion-selective membranes to become more cation selective and to have a higher effective cation-transference number. A higher cation-transference number for the neutral or anion-selective membranes would result in lower coulomb efficiency because the theoretical coulomb efficiency is the difference in the cation-transference numbers of the cation-selective and the neutral or anion-selective membranes. The fouling material that was observed on the cation-selective membranes and the cell separators probably adhered to them because of the slightly sticky nature of the fouling material. The material on the cation-selective membranes and cell separators would increase the electrical resistance of the stack, but probably would have little effect on the coulomb efficiency.

Treatments to Remove Fouling

Two types of remedial treatments were found to be helpful in removing fouling material from the stack without disassembly. They were flushing with short bursts of nitrogen and flushing with a solution of an enzyme-active laundry detergent or sodium chloride.

The procedure for nitrogen flushing was to admit three to six 1-sec bursts of nitrogen (at a pressure about 4 psi greater than the pressure of the feed solution) into the depleting compartments in a 1-min period while the normal solution-flow rates were maintained. It was hoped that the bursts of gas would cause vigorous agitation in the depleting compartment and loosen the fouling material so that it would be carried out of the compartment by the feed solution. Nitrogen was used for flushing because it was readily available under pressure, but compressed air probably would have been equally satisfactory. Nitrogen flushing had almost no effect when the stack power was on, which indicates that the fouling material was electrically charged. Nitrogen flushing with the stack power off resulted in an average reduction of about 14% in the cell-pair resistance in Runs 13-25, but did not reduce the cell-pair resistance to its original value. In these runs, the nitrogen flushing was carried out after the stack had been in operation for periods of 5 to 33 hr.

In Runs 29-39, nitrogen flushing was carried out at 20-min intervals in an attempt to prevent the membranes from becoming heavily fouled. During Runs 29-31, in which the nitrogen flushing was done with the stack power off, the average cell-pair resistance increased from cycle to cycle (a cycle was one 20-min period of operation followed by nitrogen flushing). The increase in the average cell-pair resistance over a number of cycles during a run was about 1.3%/hr. Six 1-sec nitrogen bursts were no more effective than three bursts during a flushing period. Typically, a considerable quantity of finely divided material was removed by the first burst of nitrogen, a little by the second, but practically none by the additional bursts.

In Runs 32-39, the polarity of the stack current was reversed while nitrogen flushing was being carried out. Nitrogen flushing with current reversal removed considerable quantities of material from the stack even though the stack had been flushed with nitrogen with the stack power off immediately prior to current reversal. During Runs 32-39, the average cell-pair resistance increased about 0.4%/hr. This rate of increase in cell-pair resistance was considered to be intolerable as it would result in doubling the resistance in about 10 days. It was concluded that nitrogen flushing did not provide adequate removal of membrane fouling to permit long-term operation.

Runs 56-65 were made to determine the effectiveness of removing the membrane fouling, and thus reducing the cell-pair resistance, by circulating a solution of an enzyme-active laundry material through the stack at 12-hr intervals.

The procedure for cleaning the stack was to turn off the electrical power and solution flows to the stack and then to circulate 3 gal. of a solution of an enzyme-active laundry detergent (trade name "BIZ") through the depleting compartments of the stack for 1 hr, at a solution velocity of about 10 cm/sec. The concentration of BIZ in the cleaning solution was 15 g/gal., which was that recommended for soaking laundry. When cleaning was completed, the stack was returned to service with the conditions being used for the run.

During Runs 56-65, the average cell-pair resistance after the stack was cleaned with the BIZ solution was about 1030 ohm cm^2 compared to about 1520 ohm cm^2 before cleaning, or a reduction of 32%.

In Runs 66-70, the same procedure was used for cleaning the stack except that the cleaning solution was 3 gal. of an 18% (3.5 $\underline{N}$) sodium chloride solution instead of the enzyme-active detergent solution. It was thought that solutions of high ionic strength, such as a concentrated sodium chloride solution, might break the colloidal structure of the fouling material and make it more soluble or more easily removed from the membranes. During these runs, the average cell-pair resistance after the stack was cleaned with the sodium chloride solution was about 750 ohm cm^2 compared to about 1400 ohm cm^2 before cleaning—a reduction of 46%. The cell-pair resistance of 750 ohm cm^2 was about the same as the values obtained with clean membranes and comparable operating conditions.

The coulomb efficiencies in Runs 56-70 were not significantly affected by cleaning the stack with either the sodium chloride solution or the solution of enzyme-active laundry material.

The results of the experiments discussed above indicated that flushing the stack with a 3.5 $\underline{N}$ sodium chloride solution was the most effective method for cleaning the

stack to reduce membrane fouling without disassembly of the stack. Therefore, sodium chloride flushing was used for cleaning the stack in all subsequent demineralization runs.

The effectiveness of the sodium chloride flushing in cleaning the stack was demonstrated in over 450 hr of continuous operation during Runs 97-116. The conditions and results for Runs 97-122 are given in Table 5.

The variations in cell-pair resistance and feed turbidity during Runs 97-122 are shown in Figures 7, 8, and 9. The curves in these figures are smoothed curves obtained from the data during each run. The dotted lines connect points just before and after the stack was flushed. In Runs 97-122, the interval between cleanings was increased from 12 to 24 hr in order to increase the fraction of elapsed time that the pilot plant was on stream. During Runs 97-116, the average cell-pair resistance before the stack was cleaned was 1830 ohm cm^2 and after cleaning it was 620 ohm cm^2 —a decrease of 67%. These data indicate that cleaning the stack with the sodium chloride solution was effective for removing most of the fouling material from the membranes.

In Runs 117 and 118, which were a continuation of the long-term operation, the cell-pair resistance after cleaning was about 800 ohm-cm^2 compared to values of about 620 in previous runs.

Tap water (with nothing added) was used to flush the stack in Runs 119-121, but it was less effective than the sodium chloride solution in reducing the cell-pair resistance. Sodium chloride solution was used for flushing in Run 122, but it only reduced the cell-pair resistance to 1250 ohm cm^2, compared with an average of 620 ohm cm^2 in Runs 97-116.

As discussed above, the sodium chloride cleaning procedure was effective in reducing the cell-pair resistance to about 620 ohm cm^2 after cleaning during most of the long-term operation. As shown in Figures 7, 8, and 9 the maximum cell-pair resistance reached in a run appeared to depend on the turbidity of the feed solution. In Runs 107 and 108, the turbidity of the feed increased to about

Table 5.
Conditions and Results for Demineralization Runs 97-122[a]

Run	Turbidity of feed, JTU	Current density, mA/cm²		Depletion, fractional		Cell-pair resistance,[b] ohm cm²		Coulomb efficiency,	
		Range	Average	Range	Average	Range	Average	Range	Average
97	6.5	7.0-12.4	8.9	0.14-0.33	0.20	682-1321	1066	0.57-0.81	0.65
98	4.6	6.8-14.7	8.8	0.14-0.31	0.18	545-1305	1048	0.58-0.61	0.59
99	3.4	6.6-12.8	7.4	0.12-0.32	0.15	617-1352	1155	0.54-0.72	0.57
100	2.5-3.3	6.3-10.7	8.8	0.11-0.35	0.20	595-1420	1016	0.50-0.78	0.62
101	6.0	5.9-10.3	7.1	0.12-0.34	0.19	594-1181	990	0.46-0.74	0.59
102	3.8-4.6	5.0-13.0	7.5	0.08-0.33	0.16	496-1492	1087	0.36-0.61	0.47
103	3.5	4.7-13.6	7.8	0.06-0.27	0.14	642-1603	1207	0.30-0.64	0.46
104	1.3-1.5	5.3-13.3	8.1	0.06-0.37	0.18	562-1614	1152	0.32-0.81	0.62
105	1.7-2.0	5.3-13.3	7.7	0.13-0.36	0.19	593-1728	1222	0.69-0.81	0.72
106	3.1-3.2	4.7-13.8	7.2	0.10-0.38	0.18	559-2026	1403	0.62-0.84	0.70
107	6.5-7.7	4.1-13.3	6.7	0.10-0.34	0.15	579-2320	1596	0.58-0.75	0.68
108	7.2-8.0	4.0-13.3	6.8	0.08-0.31	0.16	631-2467	1506	0.65-0.79	0.71
109	2.0-2.2	5.0-10.7	6.5	0.12-0.24	0.17	728-2052	1497	0.65-0.84	0.73
110	1.4-1.6	4.3-11.9	5.1	0.10-0.34	0.13	600-2009	1620	0.61-0.88	0.68
111	1.9-2.1	4.3-13.0	6.7	0.09-0.39	0.17	543-2091	1443	0.63-0.85	0.70
112	2.3-2.6	4.1-12.4	7.0	0.09-0.28	0.16	626-2118	1377	0.59-0.69	0.65
113	1.1-1.3	4.4-12.7	7.0	0.09-0.34	0.18	602-1738	1373	0.59-0.89	0.73
114	1.5	4.2-11.5	6.4	0.08-0.32	0.15	629-2128	1514	0.59-0.79	0.67
115	3.8-3.9	4.0-11.3	6.1	0.08-0.25	0.13	667-2364	1695	0.58-0.72	0.65
116	3.2	3.6-11.9	6.1	0.09-0.27	0.15	628-2496	1617	0.65-0.77	0.71
117	1.7-2.2	3.7-9.7	5.7	0.10-0.24	0.14	792-2091	1575	0.70-0.76	0.73
118	6.5-6.9	3.7-9.7	4.6	0.07-0.24	0.10	843-2426	1870	0.55-0.81	0.70
119	5.5-7.0	3.6-7.3	4.9	0.07-0.22	0.12	1086-2562	1935	0.59-0.91	0.73
120	6.3-8.1	3.8-7.8	5.0	0.07-0.22	0.11	1011-2401	1885	0.57-0.87	0.67
121	9.1-9.2	3.3-6.1	4.3	0.07-0.18	0.11	1277-2614	1807	0.45-0.92	0.65
122	9.4-9.6	2.9-6.8	4.1	0.05-0.13	0.07	1248-2174	1835	0.32-0.58	0.45

a. The wastewater feed was chlorinated and sand filtered, the superficial solution velocity was 10 cm/sec, the product:waste ratio was 10:1, and the stack voltage was 77 V throughout this series of runs.

b. Normalized to a feed-solution temperature of 25°C and a mean concentration of 675 mg/l (0.01 N) in the depleting compartments.

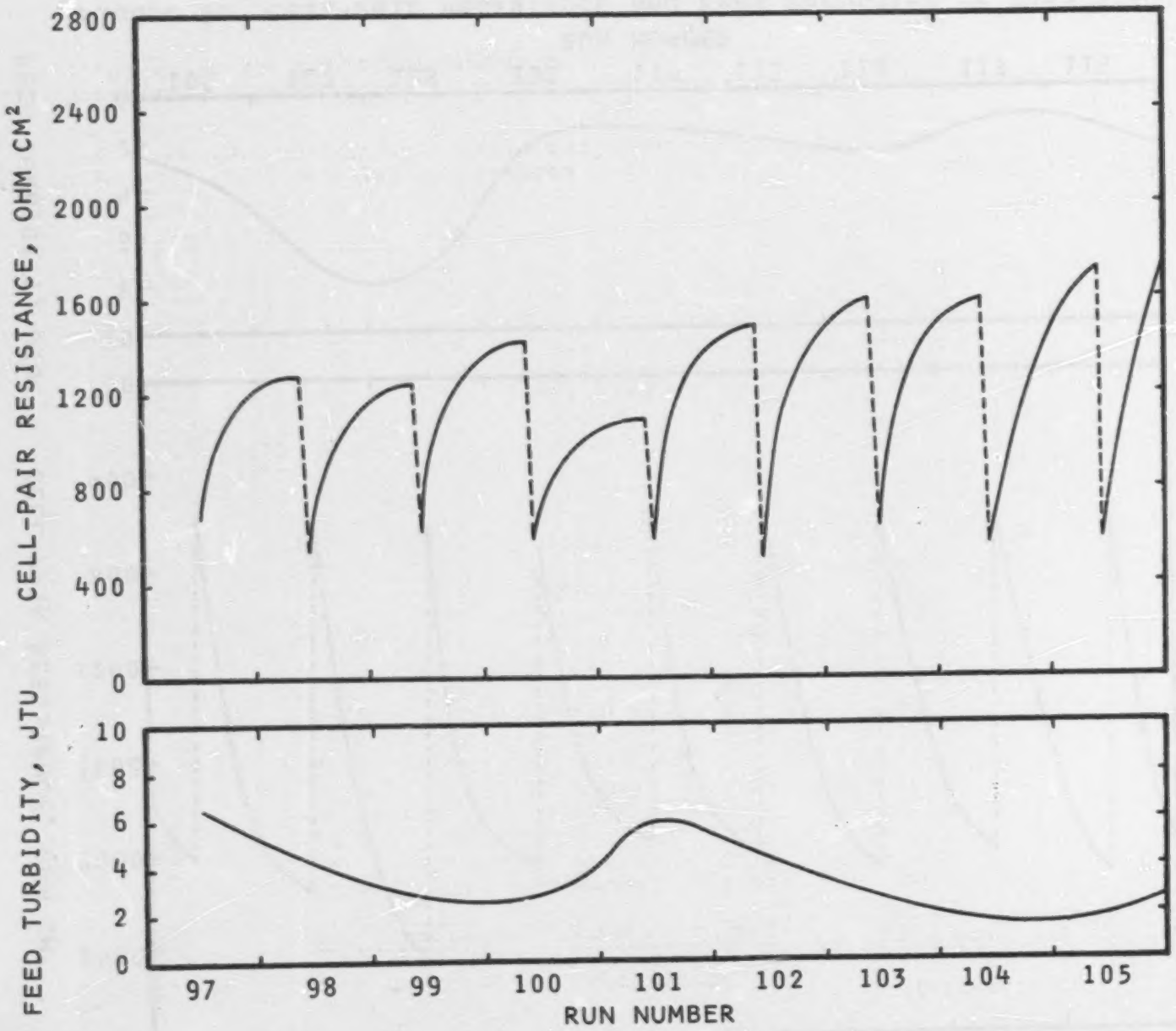


Figure 7. Cell-Pair Resistance and Feed Turbidity in Runs 97-105

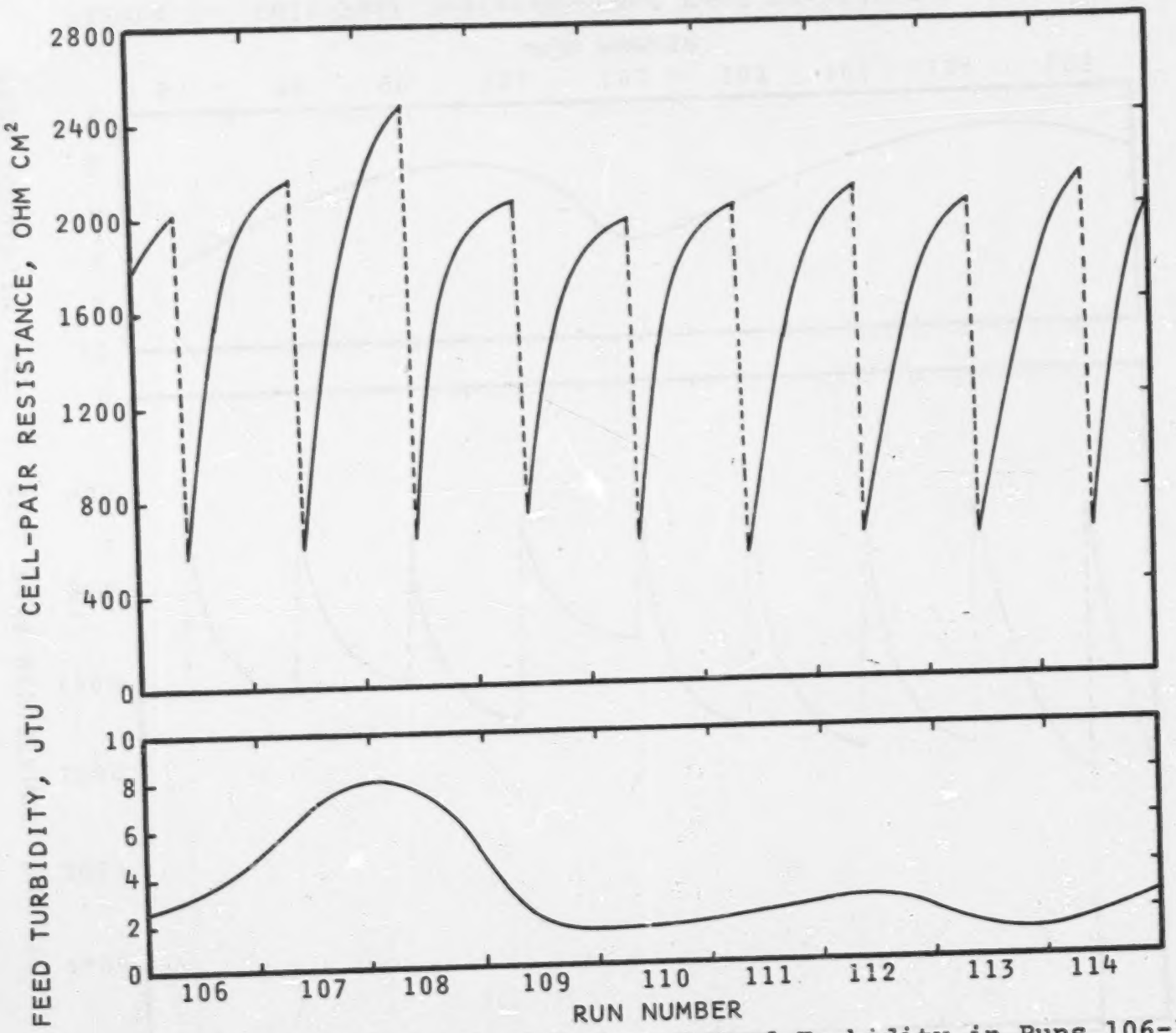


Figure 8. Cell-Pair Resistance and Feed Turbidity in Runs 106-114

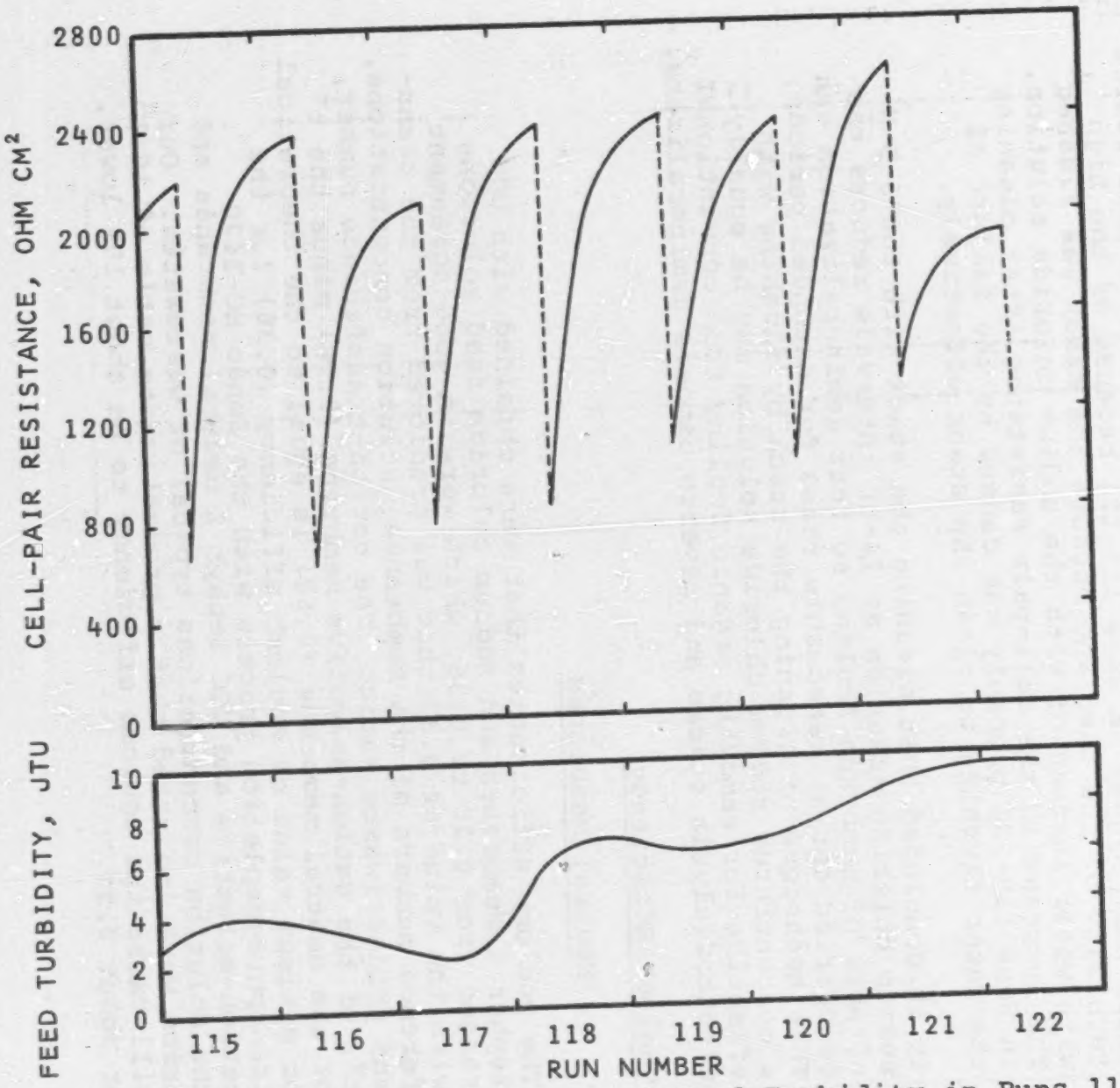


Figure 9. Cell-Pair Resistance and Feed Turbidity in Runs 115-122

8 JTU and the maximum cell-pair resistance increased to about 2400 ohm cm^2, which was higher than in any preceding runs in the series. When the feed turbidity decreased to about 2 JTU in Runs 109-114, the maximum cell-pair resistance during each run reached a fairly constant value of about 2000 ohm cm^2. The feed turbidity was high and was increasing during Runs 117-121 (Figure 9), and the maximum cell-pair resistances increased to 2400 to 2600 ohm cm^2. We believe the maximum cell-pair resistances were higher in Runs 117-121 because of the high turbidity of the feed and because the stack was flushed with water instead of with the sodium chloride solution. The increase in the cell-pair resistance after cleaning in Runs 119-121 probably was caused by the failure of the water flushing to clean the stack effectively.

It is concluded that cleaning the stack with the 3.5 N sodium chloride solution at 24-hr intervals reduces the effects of membrane fouling so that demineralization can be carried out at reasonable rates for extended periods. This technique of cleaning the stack by flushing with a concentrated sodium chloride solution may be equally effective for removing organic fouling from conventional electrodialysis stacks and reverse osmosis demineralizers.

Coulomb Efficiency

Neutral membranes

The coulomb efficiencies that were obtained with UCC Zephyr Z membranes and sodium chloride feed solutions ranged from 0.28 to 0.36, which were in good agreement with the value of 0.33 that was predicted from the transference numbers of the membranes, solution concentrations, and product:waste ratio. The cation-transference number, t^+, of the cation-selective membrane (0.98) minus the t^+ of the neutral membrane (0.62) is equal to the theoretical or maximum value of coulomb efficiency (0.36) for the transport-depletion process with the Ionac MC-3470 cation-selective and UCC Zephyr Z neutral membranes and the solution concentrations typical of wastewater. Our prior work indicated that a product:waste ratio of 10:1 will cause the coulomb efficiency to be about 10% lower, or about 0.33.

The coulomb efficiencies in Runs 28-39 with Zephyr Z membranes and wastewater decreased from 0.26 to 0.14. This decrease in coulomb efficiency indicated that membrane fouling was severely affecting the membranes. The low coulomb efficiencies obtained with the Zephyr Z membranes indicated that better membranes must be found. As discussed in the section on membranes, the properties of other membrane materials were determined in an effort to find better neutral membranes. However, none of the materials investigated appeared to be better than the Zephyr Z membranes in overall properties.

Ionac IM-12 anion-selective membranes

Ionac IM-12 anion-selective membranes were used in place of the Zephyr Z membranes in Runs 40-122. Coulomb efficiencies of 0.90 to 0.99 were obtained when 0.012 N (700 mg/l.) sodium chloride solutions were demineralized with the IM-12 membranes. A decrease in the pH of the depleted stream indicated that the limiting current density with the IM-12 membranes was about 3.5 mA/cm^2 with a solution velocity of 10 cm/sec and a product:waste ratio of 10:1. However, when the enriched stream was acidified to about pH 3 as recommended by Ionac Chemical Company, much higher current densities (6 to 10 mA/cm^2) could be used without the precipitation of pH-sensitive salts that is usually encountered with anion-selective membranes at the limiting current density.

The coulomb efficiencies obtained in the first runs with IM-12 membranes and wastewater feed (Runs 43-47) ranged from about 0.70 to 0.90. The coulomb efficiencies decreased in succeeding runs until the range of coulomb efficiencies was only 0.50 to 0.62 in Runs 81-85. The coulomb efficiencies obtained with these membranes when demineralizing sodium chloride solutions were 0.46 to 0.62, compared to the values of 0.90 to 0.99 when the membranes were new.

The stack was disassembled and the cation-transference numbers, t^+, of membranes from the stack were determined. The t^+ values for the Ionac MC-3470 cation-selective membranes ranged from 0.97 to 0.99. The average t^+ value of 0.98 for the MC-3470 membranes from the stack was the same as that for new MC-3470 membranes. The t^+ values for the Ionac IM-12 anion-selective membranes from the stack ranged from 0.26 to 0.35, with an average

value of 0.32, compared to a value of 0.05 for new IM-12 membranes. This change in the t^+ values of the IM-12 membranes would be expected to cause the maximum attainable coulomb efficiency to decrease from about 0.93 (0.98-0.05) to about 0.66 (0.98-0.32).

In an attempt to restore the original t^+ values of the IM-12 membranes, two membranes from the stack were cleaned by a procedure similar to that which is used to clean electrodialysis stacks used for demineralization of whey. The membranes were treated with a solution of hydrochloric acid (pH 2) for 20 min, rinsed with water, and treated with a solution of sodium hydroxide (pH 13) for 20 min. This cleaning procedure did not significantly change the t^+ values of the membranes.

These results indicated that the IM-12 membranes had been so badly fouled by exposure to wastewater that the fouling could not be easily removed to restore the electrochemical properties of the membranes.

New IM-12 anion-selective and MC-3470 cation-selective membranes from Ionac Chemical Company were installed in the stack before the long-term operation (Runs 97-122) was begun. As shown by the data in Table 5, the average coulomb efficiency decreased from 0.65 in Run 97 to 0.46 in Run 103, so that the average coulomb efficiency for Runs 97-103 was 0.57. The sodium chloride solution used to flush the stack in Run 104 was acidified to pH 2.5 with hydrochloric acid. The coulomb efficiency increased to 0.70 after this flushing and remained in the range of 0.65 to 0.73, for an average value of 0.70, during Runs 105-118, although unacidified sodium chloride solutions were used for flushing the stack in all of these runs. (The addition of the acid to the sodium chloride cleaning solution did not appear to enhance its efficacy in reducing cell-pair resistance even though the coulomb efficiency was increased.)

The coulomb efficiencies decreased slightly to an average of 0.68 in Runs 119-121, in which the stack was flushed with water containing no sodium chloride. Flushing the stack with sodium chloride solution in Run 122 did not restore the coulomb efficiency to its previous level.

We conclude that average coulomb efficiencies of about 0.70 can be maintained during long periods of operation when demineralizing wastewater with Ionac IM-12 and MC-3470 membranes if the stack is flushed at 24-hr intervals with an 18% (3.5 N) sodium chloride solution.

Alum Pretreatment of Wastewater

Runs 75-85 were made to determine whether alum treatment of the wastewater would significantly reduce the problems of fouling in the depleting compartments of the stack. An alum solution containing 75 g/l. of commercial "17% alum" was added continuously to the incoming wastewater stream with a metering pump as the water flowed into the 300-gal. tank. The tank provided a retention time of about 90 min to permit flocculation by the alum. The alum-treated wastewater flowed from the flocculation tank to the sand filters and feed-solution system. The total dissolved solids concentration of the wastewater was increased to about 800 mg/l. by the addition of calcium chloride, sodium sulfate, and sodium bicarbonate.

The alum solution was added at a rate to give a concentration of 30 mg/l. of alum (as aluminum sulfate) in the incoming wastewater. This concentration of alum reduced the turbidity of the wastewater to about 0.6 JTU in laboratory jar tests. The stack was cleaned at 24-hr intervals by flushing with a sodium chloride solution in the usual manner.

The data for Runs 78-85 (with alum-treated wastewater) show that the cell-pair resistances after the stack was cleaned ranged from about 680 to 970 ohm cm^2. These values are about the same as the range of 600 to 900 ohm cm^2 (after cleaning) which was found in Runs 66-69, which were made without alum treatment of the wastewater. Also, there was little difference between the coulomb-efficiency range of 0.43 to 0.65 (after cleaning) in Runs 78-85 and the range of 0.45 to 0.60 (after cleaning) in Runs 66-69. The results from these runs indicated that, although pretreatment with alum reduced the turbidity of the feed solution entering the stack, it did not significantly reduce the problem of fouling in the stack.

Effect of Removing Spacer Screens from Depleting Compartments

Runs 86-89 were made to determine whether removing the spacer screens from the depleting compartments would facilitate removal of the fouling material from the compartments by flushing. The screens were removed from the depleting-compartment spacer frames, leaving only the perimeter gaskets and the distribution disks. During assembly of the stack, proper location of the distribution disks was maintained by the use of guide tubes which were removed after the stack assembly had been clamped together. The other conditions for Runs 86-89 were the same as those described above for Runs 78-85, including alum treatment of the wastewater. During Runs 86 and 87, the hydraulic pressure in the depleting compartments was maintained 3 psi higher than the pressure in the enriching compartments to keep the membranes from touching and reducing the solution flow rate through the depleting compartments. In Runs 88 and 89, the pressure differential was increased to 6 psi.

The results from Runs 86-89 showed that operation without spacer screens in the depleting compartments resulted in generally slightly higher cell-pair resistances, before cleaning, than the corresponding values in Runs 78-85 (with spacer screens).

However, the cell-pair resistances after cleaning were significantly higher in Runs 86-89, without spacer screens, than in Runs 78-85 with spacer screens. The coulomb efficiency values were slightly lower in the runs without spacer screens than in the runs with spacer screens.

These results indicate that removing the spacer screens from the depleting compartments made the flushing less, rather than more, effective for removing the fouling material from the compartments. It is probable that the higher cell-pair resistances that were obtained when the screens were removed were a result of the presence of high-resistance depleted boundary layers in the depleting compartments. The spacer screens promote turbulence in the solutions, which tends to decrease the thickness of the boundary layers and reduce the cell-pair resistance.

Effect of Solution Velocity and Product:Waste Ratio

Runs 94-96 were made to determine the effect of changes in solution velocity and product:waste ratio on cell-pair resistance and coulomb efficiency. The feed solution for these runs contained about 810 mg/l. of sodium chloride in Birmingham tap water. The wastewater feed solution was not used for these experiments because membrane fouling caused rapid changes in cell-pair resistance and other parameters, which would have masked the variations caused by the changes in solution velocity and product:waste ratio. The conditions for and results of Runs 94-96 are given in Table 6.

Table 6
Conditions for and Results of
Demineralization Runs 94-96

Run	Solution velocity, cm/sec	Product: waste ratio	Current density, mA/cm^2	Cell-pair resistance,[a] ohm cm^2	Coulomb efficiency
94	5	10:1	5.4	261	0.86
95-A	14	10:1	11.9	327	0.88
-B	10	10:1	9.6	319	0.84
-C	10	5:1	9.0	333	0.74
96-A	10	15:1	9.3	330	0.83
-B	10	10:1	9.2	343	0.82

a. Normalized to a feed solution temperature of 25°C and a mean concentration of 585 mg/l. (0.01 M) of sodium chloride in the depleting compartments.

The data in Table 6 show that coulomb efficiencies of about 0.83 and cell-pair resistances of about 320 ohm cm^2 were generally obtained. However, in Run 94, with a solution velocity of 5 cm/sec, the cell-pair resistance was only 261 ohm cm^2; and in Run 95; with a product:waste ratio of 5:1, the coulomb efficiency was only 0.74. The reason for these two anomalous results is not known. Because of the generally small variations in coulomb

efficiency and cell-pair resistance observed with the various conditions, it was concluded that variations in solution velocity from 5 to 14 cm/sec and in product:waste ratios from 5:1 to 15:1 had little effect on cell-pair resistances or coulomb efficiencies.

Ion-Removal Selectivity

In the transport-depletion process, all ions are not necessarily removed from the feed solution to the same degree. The fraction of each ion that is removed depends on the solution composition and the types of membranes used.

Chemical analyses were made on seven sets of feed and product samples taken during approximately 600 hours of continuous pilot-plant operation with Ionac IM-12 anion-selective membranes (Runs 97-122). Ion-selectivity data from these seven sets of samples are given in Table 7. The fractions of all ions removed were based on the total normalities of the corresponding feed and product samples assuming no ions other than those shown were present in significant quantities. The combination of Ionac MC-3470 cation-selective and Ionac IM-12 anion-selective membranes had significantly higher selectivity for the removal of bicarbonate and calcium ions than for other ions. The lowest selectivities were for the removal of sodium and phosphate ions. Although there was considerable scatter in the data, the results indicate that there was no significant change in the ion-removal selectivity during the approximately 600 hours of continuous operation with these membranes. This indicates that the membrane fouling that caused an increase in stack resistance had little effect on the selectivity characteristics of the membranes.

Only a few chemical analyses were made of the demineralized (or product) wastewater from runs with the Zephyr Z membranes. The results of the analyses that were made indicated that there was no significant selective removal of any ion.

Table 7
Ion-Removal Selectivity[a]

Ion	Fraction of specific ion removed divided by fraction of all ions removed	
	Average	Range
Bicarbonate	1.42	1.33-1.49
Calcium	1.21	0.97-1.41
Ammonium	1.00	0.60-1.20
Potassium	0.92	0.56-1.70
Magnesium	0.62	0.16-1.09
Sulfate	0.80	0.52-0.94
Chloride	0.67	0.57-0.83
Sodium	0.56	0.38-0.74
Phosphate	0.36	0.04-1.36

a. Based on analyses of seven sets of samples.

ECONOMIC CONSIDERATIONS

The results obtained in our pilot-plant operations with IM-12 membranes indicate that cleaning the stack with a sodium chloride solution makes continuous operation practical with feed water having a turbidity in the range of 1 to 10 JTU. Occasional shutdowns to permit more thorough cleaning of the stacks might be necessary.

Estimates of the costs of demineralization using the fouling-resistant IM-12 membranes were made for comparison with those published by Brunner[1] for demineralization of wastewater using electrodialysis membranes designed for treatment of brackish water. The same conditions were assumed insofar as was possible when making the estimates. Our cost estimates were made with the same assumptions about the costs of piping, instrumentation, contingencies, and similar items so that they could be compared directly with the costs given by Brunner. The prices of equipment and materials were obtained from published information or quotations from suppliers. It was assumed for both cases that some degree of coagulation and clarification of the secondary wastewater would be required and that activated-carbon pretreatment would be required for brackish water membranes but not for the IM-12 membranes. No credit was given for the improved water quality obtained when carbon treatment is used.

The operating conditions used for the cost estimates were based on the data obtained in our pilot plant during approximately 600 hours of operation during Runs 97-122. The coulomb efficiency assumed for the cost estimates was 0.70, which was the average value obtained in Runs 105-118. A conservative value of 500 was assumed for the polarization parameter, $i/\underline{N}$, (current density in mA/cm^2, divided by the log mean normality in the depleting compartments) although the average value obtained in Runs 97-118 was 620. The assumed cell-pair voltage of 7.1 volts was the average value in Runs 97-118.

Preceding page blank

The other conditions assumed for the cost estimates were:

solution velocity - 10 cm/sec
product:waste ratio - 10:1
production rate - 10 mgd for 365 days/yr
cation-selective membranes - Ionac MC-3470
anion-selective membranes - Ionac IM-12
membrane cost - $3/ft^2
total dissolved solids concentration in feed water - 850 mg/l.
total dissolved solids concentration in product water - 500 mg/l.
average equivalent weight of dissolved salts - 67.5
feed-water temperature - 25°C
feed-water turbidity - 1 to 10 JTU

The feed water was assumed to have a composition similar to that used in our pilot-plant studies. It was assumed that the stacks would be flushed with an 18% sodium chloride solution for 1 hr at 24-hr intervals.

The details of the capital costs are given in Table 8. For the IM-12 membrane system, 198 stacks, each with 150 cell pairs, would be required. For the cost estimates this number was increased by 15%, to 228 stacks, to provide spare stacks for use during periodic maintenance of others. The quoted price of the stacks without membranes was $5265 each. Membranes (at $3/ft^2) cost $3883 per stack, increasing the total cost to $9148 per stack. For the brackish water membrane system, stack costs are those of a different manufacturer and date back to 1966. These were not updated and are likely to be slightly low.

The rectifier capacity needed for the IM-12 membrane system would be 2900 kw, compared to 370 kw for the brackish water membrane system because of the lower coulomb efficiency and higher cell-pair resistance values of the former.

The size of the building to house the IM-12 membrane system was based on an area of 30 ft^2 per stack, which a floor plan of the projected plant indicated was more than adequate for the type of stacks used.

Table 8.
Capital Costs for 10 mgd Demineralization Plant

Item	Cost, $ IM-12 membranes	Cost, $ Brackish water membranes[a]
Electrodialysis stacks with membranes	2,085,700	1,557,200
Installation - 15% of component cost	312,900	233,600
Rectifiers - installed	203,000	43,900
Pumps and motors - installed	73,000	98,500
Piping - 30% of installed cost of stacks and pumps	741,500	566,800
Instrumentation and controls - 10% of stacks and pumps	247,200	188,900
Acid storage tank	11,000	11,000
Building - at $13/ft^2	177,800[b]	114,300[c]
Contingencies - 10% of investment	385,200	281,400
Engineering - 5% of above	211,900	154,800
Interest on investment during construction - 4% of above	178,000	130,000
Total capital cost	4,627,200	3,380,400

a. See Reference 5.

b. Assumed 30 ft^2/stack.

c. Assumed 100 ft^2/stack.

The details of the operating costs are given in Table 9. The costs of disposal of the concentrated waste stream and of flocculation and filtration are not included because these costs were considered to be common to both processes. The estimated cost of electrical energy with the IM-12 membrane system is about 4.3¢/kgal higher than with brackish water membranes because of the lower coulomb efficiency and higher cell-pair resistance. The estimated cost of sodium chloride used to flush the stack was based on the concentration and quantity used in our pilot-plant studies. In the pilot plant 1.31 lb of sodium chloride was used per kilogallon of product water, and the cost of the sodium chloride, at 1.3¢/lb was 1.7¢/kgal of product water. We did not attempt to determine the minimum amount or concentration of sodium chloride solution that was effective in cleaning the stack. In a larger installation, the cost of sodium chloride could almost certainly be reduced several-fold by the use of a smaller volume of the sodium chloride solution relative to the volume of product water or by reusing the solution. We believe the cost of 1.7¢/kgal for sodium chloride given in Table 9 in very conservative.

The amortization costs given in Table 9 were based on a 25-yr period at 6% interest to make them more realistic. The amortization cost based on 25 years and 4% interest given by Brunner was updated to a basis of 25 years and 6% interest so that the two estimates would be more nearly comparable.

The most recent data that was available on the costs of activated-carbon treatment of wastewater was that given by Smith and McMichael.[6] They estimated the total treatment costs for a 10 mgd activated-carbon treatment plant to be 10.1¢/kgal and the capital cost of the plant to be $1,600,000. An adjustment of the amortization costs from their basis of 4.5% for 25 yr to the basis of 6% for 25 yr increased the amortization cost from 3.0¢/kgal to 3.4¢/kgal and increased the total estimated cost of activated-carbon treatment to 10.5¢/kgal.

With these considerations, the estimated total cost for demineralizing secondary wastewater by the IM-12 membrane system is 25.7¢/kgal compared to 27.8¢/kgal by the brackish water membrane system with activated-carbon pretreatment.

Table 9.
Operating Costs for Demineralizing 10 mgd of Secondary Wastewater

Item	Cost, ¢/kgal of product water	
	IM-12 membranes	Brackish water membranes[a]
Electric energy		
Rectifier energy at 90% rectifier efficiency and power at 0.7¢/kwh	5.18	0.69
Pumping energy at 0.7¢/kwh	0.16	0.32
Other energy (negligible)	-	-
Sulfuric acid	0.72	1.56
Sodium chloride - for flushing stack, at 1.3¢/lb	1.70	-
Maintenance		
Membranes (4 sets over 25 yr)	3.82	3.23
Spacers (1 set over 10 yr)	1.89	2.00
Anodes	0.25	0.48
Other materials (0.5% of remaining capital cost/yr)	0.28	0.25
Labor (0.5% of capital cost/yr)	0.62	0.46
Operating labor (three operators at $6,000/yr and one operator and coordinator at $8,000/yr)	0.71	0.71
General and administrative overhead (30% of labor cost)	0.40	0.35
Amortization of equipment (25 yr at 6% interest)	9.92	7.24[b]
Total operating costs	25.65	17.29
Activated carbon pretreatment	0.0	10.5
Total cost exclusive of flocculation, filtration, and waste disposal	25.65	27.79

a. See Reference 5.

b. Updated to 6% interest from 4% used by Brunner.

The slightly higher cost for demineralization by conventional electrodialysis is primarily due to the high cost of the activated-carbon pretreatment. If the technique of flushing with sodium chloride solution is as effective in cleaning brackish water membrane stacks as it is in cleaning the IM-12 membrane stacks, activated-carbon pretreatemnt probably could be eliminated and the total operating cost of the brackish water membrane system might be lower than for the IM-12 membrane system.

ACKNOWLEDGMENTS

This research was directed by Mr. Robert E. Lacey and Mr. Edward W. Lang, and was carried out by Mr. Everett L. Huffman with the aid of Mr. Samuel L. Edward.

The cooperation and assistance of Mr. H. A. Snow, Jefferson County Engineer, and Mr. W. M. McInnis, Superintendent of the Shades Valley Sewage Treatment Plant, are gratefully acknowledged.

The support of this study by Water Quality Office Contract No. 14-12-812 and the advice and assistance of Dr. Carl A. Brunner, Project Officer, are also acknowledged.

REFERENCES

1. C. A. Brunner, J. Water Pollution Control Federation, 39, 10, Part 2, R1 (Oct., 1967).

2. Southern Research Institute, "Demineralization by Transport Depletion", Office of Saline Water Research and Development Report 80 (1963).

3. Southern Research Institute, "Development of Transport-Depletion Processes", Office of Saline Water Research and Development Report 439 (1969).

4. Bureau of Reclamation, "Test Manual (Tentative) for Permselective Membranes", Office of Saline Water Research and Development Report 77 (1964).

5. A. J. Casolo and F. B. Leitz, 133rd National Meeting of the Electrochemical Society, Boston, Massachusetts, May, 1968.

6. Robert Smith and W. F. McMichael, "Cost and Performance Estimates for Tertiary Wastewater Treating Processes", Report No. TWRC-9, Robert A. Taft Water Research Center, FWPCA, Cincinnati, Ohio, (June, 1969).

Preceding page blank

1 Accession Number	2 Subject Field & Group	SELECTED WATER RESOURCES ABSTRACTS INPUT TRANSACTION FORM
	03A	

5 Organization

Southern Research Institute
Birmingham, Alabama

6 Title

DEMINERALIZATION OF WASTEWATER BY THE TRANSPORT-DEPLETION PROCESS

10 Author(s)

Lacey, Robert E., and
Huffman, Everett L.

16 Project Designation

FWQA Contract Nos. 14-12-443 and 14-12-812

21 Note

22 Citation

Final report to Water Quality Office under Contract Nos. 14-12-443 and 14-12-812, February, 1971. 86 p, 9 tab, 9 fig, 5 ref.

23 Descriptors (Starred First)

*Desalination processes, *Transport depletion, *Wastewater treatment
*Electrodialysis, Demineralization, Membrane processes, Sewage effluents

25 Identifiers (Starred First)

27 Abstract

The transport-depletion process was investigated for demineralizing municipal secondary effluent. Wastewater containing 850 mg/l. total dissolved solids and having a turbidity of 1 to 10 JTU, was demineralized continuously for 500 hours in a pilot plant at a rate of 3800 gpd.

Although regenerated-cellulose membranes were found to be satisfactory in regard to physical durability, the coulomb efficiencies attained with these membranes were only 0.14 to 0.28. The major problems encountered in demineralization of wastewaters by conventional electrodialysis, fouling and scaling, were, however, largely overcome by the use of a special anion-selective membrane and periodic flushing of the stack with sodium chloride solution. With the special anion-selective membrane, current densities up to three times the conventional limiting current density could be used without precipitation of pH-sensitive salts and coulomb efficiencies of 0.70 were obtained during the 500 hours of operation.

Membrane fouling, which caused the electrical resistance of the demineralizer stack to increase, was largely overcome by flushing the stack with a sodium chloride solution. This flushing technique should be useful for cleaning conventional electrodialysis stacks.

Cost estimates for a 10 mgd plant indicated a demineralization cost of 25.7¢/kgal for transport depletion compared to 27.8¢/kgal for electrodialysis and required activated-carbon pretreatment. The estimated cost for transport depletion is slightly lower because it does not require activated-carbon pretreatment.

This report was submitted in fulfillment of Contract Nos. 14-12-443 and 14-12-812 under the sponsorship of the Water Quality Office of the Environmental Protective Agency.

Abstractor	Institution
Everett L. Huffman	Southern Research Institute, Birmingham, Alabama

WR:102 (REV. JULY 1969)
WRSIC

SEND TO: WATER RESOURCES SCIENTIFIC INFORMATION CENTER
U.S. DEPARTMENT OF THE INTERIOR
WASHINGTON, D. C. 20240

* GPO: 1969-359-339